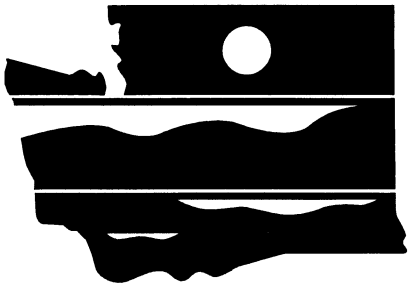

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Field Sampling and Measurement Protocols for the Watershed Assessments Section

November 1993

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Field Sampling and Measurement Protocols for the Watershed Assessments Section

by
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CONTENTS

1. SAMPLE CONTAINER RINSING PROTOCOLS

Should you rinse sample containers before sampling? The laboratory believes it is not necessary to rinse sample containers, because they are rigorously cleaned and should not have any active sites on the inner sides which could adsorb particles. EILS Ambient Section monitored their field and lab variability with respect to rinsing and found no difference between field rinsed and non-rinsed samples. Considering this information, it may not be necessary to rinse sample containers. However, the project manager should decide on a consistent protocol considering sample type, sample location, potential contamination, and logistics.

NOTE: Never rinse bacteria bottles or those which contain preservative.

If a sampling device such as a Van Dorn, Kemmer bottle, automatic sampler, or bucket is used to collect a sample, make sure the device is thoroughly cleaned and rinsed before sampling. Cleaning and rinsing protocols for all sampling devices are dependent on the specific variable(s) being measured. The laboratory can provide guidance.

2. NUTRIENT SAMPLING PROTOCOL FOR:

Ammonia (NH_3)
Nitrate-Nitrite (NO_3-NO_2)
Total Persulfate Nitrogen (TPN)
Total Phosphorus (TP)
Nutrients 3 (NH_3, NO_3-NO_2 and TP)

Introduction

Nutrients are very sensitive to contamination, especially phosphorus, which can occur at extremely low concentrations. Handle with care while sampling.

Nutrient sample containers contain acid as a preservative. The acid lowers the pH of the sample, keeping the nutrients from reacting with the other chemicals in the water and preventing decomposition. It is important to keep all the acid inside the bottle. Do not rinse the bottle or allow any sample to overflow.

Sample Bottles

Clear 125 mL polyethylene with sulfuric acid preservative (H_2SO_4), provided by the lab.

Sample Storage

4°C, in the dark.

Holding Time

48 hrs up to 28 days depending on parameter. Refer to Lab User's Manual for more detail.

Sampling procedure

Collecting surface samples:

1. Unscrew the bottle lid, and place it on top of the bottle at an angle so an opening of 1/4 to 1/2 inch remains. Hold the lid in place with your index finger, as far from the opening as it can be.

2. Facing upstream, quickly submerge the bottle below the surface and make a large sweeping motion across the water in front of your body. Check how full the bottle is.

3. Repeat the motion again if necessary, filling the bottle to the shoulder. Do not fill the bottle to overflowing, as this will dilute the acid. If the bottle overflows by just a few mLs, it is probably not going to affect the pH of the sample. If the sample overflows by half the sample volume, replace the bottle if you can. If not, make a note to the lab to check the pH of the sample before analysis (Smith, 1992). Cap bottle immediately.

Sampling from a bridge or pouring water into the bottle:

Try not to overfill the bottle. You don't want to lose any of the preservative. If you do, follow the steps in No. 3, above.

References

Manchester Laboratory User's Manual, 1991

Standard Methods, 17th edition

Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound, ed. 10/9/91.

Personal communication with selected WAS staff, 1/30/92.

Smith, Craig. Personal communication, March 31, 1992.

3. ORTHOPHOSPHATE SAMPLING AND FILTERING PROTOCOL

Introduction

There are two alternatives for filtering the orthophosphate (PO_4) samples. (See following pages for sampling and filtering procedures). The following options are recommended to reduce the chances for contamination.

1. Filter in the wet lab or vans. If samples are filtered in the wet lab or vans, collect the samples in larger container and then filter into a 125 mL Ortho-P brown bottle, or collect two 125 mL samples and use one for rinsing filtering device before collecting filtrate for analysis.

   Collecting samples in only one of the small bottles introduces a chance for contamination, because there is not enough sample to both rinse the filtering apparatus and collect a sample. A larger sample volume will allow for thorough rinsing of the filtering apparatus before collecting the filtrate for analysis. If one opts for using larger bottles for sample collection, they must be properly cleaned (washed with non-phosphate detergent, then acid-rinsed with HCl). The lab does not have the time or space to do the cleaning, so the investigator will have to do it themselves. This may be too labor and space intensive for some projects.

2. Filter in the field using a syringe and syringe filter. This is a very efficient and clean procedure for collecting orthophosphate samples and is the best procedure of the two options listed here for avoiding contamination and meeting the operational definition of dissolved reactive phosphorus. (Recommended procedure)

The following is a description of boatshed/van filtering procedures.

Sample Bottle

125 mL amber polyethylene

Sample Storage

4°C in the dark

Holding Time

Filter sample immediately after collection
48 hours total from sample collection to analysis

Sampling Procedure

The amber bottles have been treated specifically for nutrient sampling. Do not use other bottles for taking the sample before filtering; the potential for contamination is too great.

1. Sample may be taken with the lid completely off. It does not matter whether the bottle overflows or not.

2. Do not rinse the bottle.

3. Filter sample immediately after collection following the procedure listed below.

Filtering Procedure

Equipment:
peristaltic pump
tubing
filter apparatus (stand, polyethylene mesh support screens, under-drain and over-drain supports, o-ring, wing nuts)
filters, millipore HATF, 0.45 mm pore size
squirt bottle with deionized (DI) water for rinsing
large bottle of DI water for filter rinsing
10% HCl

1. Order the samples as best you can from low to high orthophosphate concentration prior to filtering. This ensures the least chance of contamination between filtered samples.

2. Set up the filtering apparatus without a filter. Cycle 10% HCl through the system for 60 seconds (acid used for acid-washing can be reused). Rinse by running DI water through the apparatus for 60 seconds.

3. Place a paper filter in the apparatus using clean stainless steel forceps. If forceps are not available, handle it only by the edges. Wet the filter with DI water after it is in place, as a pre-rinse, and to hold it in place. Make sure the wing nuts are tight enough to prevent leakage through the sides.

4. Rinse the filter by running approximately 1 liter of DI water through it. This ensures that the filter wetting agents and any other contamination washes through. Run a filter blank (see Quality Assurance, below).

5. Remove the intake tube from the DI water and allow all remaining water to pass through the filter plate.

6. Place the tube in the sample bottle. Allow approximately 100 mL to run through before collecting the filtered sample in a clean 125 mL brown (amber) bottle.

7. Rinse the end of the intake tube with DI water to prevent contamination of rinse water. When the tube is not in use, be sure not to let it touch any unclean surfaces; have an extra bottle to place it in. The bottle can be empty, or filled with DI water.

8. Place the intake tube into the DI water, and allow approximately 200 mL to run through before filtering the next sample.

9. If the filter clogs, replace it. Run a filter blank first (see below). Make sure not to interchange the two plastic support screens on either side of the filter. The top one will only have contact with filtrant, the lower only with filtrate. Follow the procedures from 3, above.

10. When done processing samples, take the filter out, and rinse the apparatus with approximately 200 mL of DI water. Disassemble and store in its proper box in its proper location in the boatshed.

Quality Assurance

When filtering samples, collect filter blanks to ensure that samples are not being contaminated by the filtering apparatus. At least two filter blanks should be run for each filter used: one just prior to filtering the samples, and one either before replacing the filter or after all samples have been run. If a large number of samples are to be filtered, run a filter blank after each 10 samples. If the filter is clogging before 10 samples have been run, run filter blanks more often. Filter blanks consist of DI water run through the filtering apparatus.

Much of the literature reviewed on filtering recommended changing the filter between each sample. However, data collected by WAS staff seems to indicate that changing the filter only every 10 or so samples, or when the filter becomes clogged, does not have a significant impact on the level of PO_4 in the sample.

The following is a description of syringe filtering procedures.

Sample Bottle

same as above

Sample Storage

same as above

Holding Time

same as above

Sampling and Filtering Procedure

1. Remove plunger from 60 cc syringe and rinse syringe and plunger 3 times with sample water.

2. Attach 0.45 μ syringe filter to syringe.

3. Collect sample in syringe chamber and replace plunger. (Fill the syringe chamber as full as possible)

4. Discard the about 20 cc of filtrate, then filter the remainder of the syringe into the 125 mL amber polyethylene sample bottle.

Quality Assurance

Collect at least one filter blank per sampling day and/or sampling team.

References

APHA. Standard Methods, 17th Edition, 1989.

Hallock, Dave, Dept. of Ecology. Protocols for Field Sampling of Nutrients, Nov. 1988.

Illinois EPA, Division of Water Pollution Control, Planning Section. Quality Assurance and Field Methods Manual, 1987 Revision.

Magoon, Stuart. Personal communication, Manchester Environmental Laboratory (MEL), 3/17/92.

Strong, Despina. Personal communication, MEL, 2/25/92.

Thomson, Dave. Personal communication, MEL, 2/11/92.

U. S. EPA. Puget Sound Protocols, February 1990.

USGS Western Region. Guidelines for the Collection, Treatment and Analysis of Water Samples, September 1990.

4. FECAL COLIFORM BACTERIA PROTOCOL FOR FRESHWATER

Introduction

There are two standard methods for the detection of coliform bacteria, the Membrane Filter technique (MF) and the Most Probable Number (MPN) index. The MF and MPN methods are not comparable; statistical comparisons of the two techniques show that MF is more precise (APHA 1989). However, MPN is better for use in chlorinated effluents, highly turbid waters (MF can be used if sample is diluted) and salt or brackish waters. The MF technique is the most common laboratory procedure for fresh water, and the analytical method most often used by EILS.

Guidance on which method to use and sampling strategy (to better understand variability between and within the methods) are still being developed.

Special Considerations:

The laboratory needs to prepare medium for bacterial analysis. It is especially important that sampling is prearranged with the lab.

Sampling for bacteria on Thursday through Sunday must be preapproved with the laboratory.

Since there are two possible methods, data should be recorded with an appropriate citation of which method was used.

If the water is extremely turbid (<25 mL can be filtered) the MPN method is necessary. Call the lab as soon as possible so they can prepare for this method.

Sample Bottles

250 mL (minimum) sterilized glass with polypropylene stopper covered with aluminum foil.

500 mL sterilized glass can be used for split samples, or if the smaller sized bottles are not available.

Bottles with yellow stickers on top contain sodium thiosulfate. These are used when chlorine is suspected to be present in the sample (thiosulfate will not affect samples if

chlorine is not present). The stopper should have masking tape with black lines, which means the bottle has been autoclaved.

If high metal contamination is suspected, bottles must have EDTA added. This is a special request and must be set up through the laboratory.

Bottles have a holding time -
3 months for bottles without thiosulfate/EDTA
1 month for bottles with thiosulfate/EDTA

Sample Storage

Cool to 4°C immediately. Store in the dark; fecal bacteria are sensitive to light.

Holding Time

Analyze within 30 hours (recommended holding time is 8 hours, however, because of logistical constraints EPA and our lab allow up to 30 hours.)

Sampling Procedure

DO NOT RINSE THE BOTTLE
DO NOT POUR WATER INTO THE FECAL BOTTLE FROM ANOTHER CONTAINER

1. Take the cork out of the bottle just before sampling, leaving the aluminum foil over the cork. Be careful not to contaminate the cork or the inside of the bottle with your fingers, dirt particles, or dripping water from bridges, etc..

2. Facing upstream, sample 6 - 12 inches below the surface, preferably in the portion of the channel with predominant flow. Avoid stirring up the sediment as this can change the results drastically. DO NOT RINSE THE BOTTLE.

3. For grab samples: Hold the bottle near its base, plunge it (mouth down) below the surface, avoiding the top microlayer where bacteria tend to concentrate. While under water, turn the bottle into the current and away from you, the shore,and the side of the sampling platform or boat. (If you are sampling from a boat, avoid gas and oil contamination. Hold the bottle upstream while the boat moves forward). Be sure to pour out enough sample to allow 1 - 2 inches of air space above each sample for

proper mixing of the sample before analysis at the lab. If you are using a bottle which contains an additive you will want to be careful to pull the bottle out of the water as it reaches the point where it is filled to 1 - 2 inches below the top. However, if overfilling does occur the sample is not lost. The thio and EDTA that Manchester puts in is in excess, but extra care not to overfill would be preferable.

4. If using the specialized bridge sampler: take out the cork just before lowering the sampler-with-bottle down on the rope. Hold the cork via the aluminum foil, or set the cork somewhere free of dirt or other sources of contamination. Lower the sampler in such a manner so as not to contaminate the open bottle with dirt or dripping water. When approaching the water surface, drop the sampler quickly through the surface to avoid the microlayer. Keep the bottle submerged long enough for the bottle to fill (or 1 - 2 inches below the top). Pull up the sampler and bottle, careful not to contaminate the sample with dirt or water from either the rope or bridge, etc.. Pour out sample to allow for the air space needed for proper mixing at the lab. Replace the cork with aluminum cover securely.

References

APHA, 1989. Standard Methods for the Examination of Water and Wastewater.

EPA, 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater.

EPA, 1978. Microbiological Methods for Monitoring the Environment.

Harris, Stephanie. EPA microbiologist at Manchester Laboratory. Personal Communication April 7, 1992.

Huntamer and Hyre, 1991. Manchester Environmental Laboratory, Laboratory Users Manual.

Jensen, Nancy. Manchester microbiologist. Personal Communication, 3/92.

Puget Sound Protocols, 1990. Recommended Protocols for Measuring Conventional Water Quality Variables and Metals in Fresh Water of the Puget Sound Region.

5. TEMPERATURE PROTOCOL

Introduction

There are many types of instruments that measure temperature, including mercury (Hg) thermometers, alcohol thermometers, and thermistors. The investigator should make sure that the instrument chosen meets their project accuracy and precision requirements. All the instruments discussed below are available somewhere in EILS.

The Hg thermometer seems to be preferred by most WAS staff because it doesn't rely on electronics, and is simple to use. The major disadvantages are that they break easily and Hg is hazardous.

The alcohol thermometer is recommended by Craig Smith (at Manchester Lab) as a possible alternative to the Hg thermometer. Their accuracy is only good within a small range, but if they break, the waste is not a problem.

Thermistors are expensive and need to be handled carefully to prevent electronic malfunctions. Their accuracy is good and EILS has a number of them available in the boatshed.

The temperature readings from the pH meters (thermistor), in the experience of most WAS staff, are always different than the Hg temperature. Part of the problem with using the pH meter temperature readings are that the readings are not normally taken directly in the water body, which is where the temperature reading should be taken for the best result.

Equipment

Hg thermometer, with metal case to reduce the chance of breakage in the field, and a scale marked every 0.1°C; or

alcohol thermometer; or

thermistor. More expensive, but doesn't break as easily, and no waste if it does. See thermistor instructions for information on handling and use.

Calibration

Check all temperature instruments at the beginning of a project against a thermometer certified by the National Institute of Standards and Technology (NIST) (Smith, 1992).

Sampling Procedure

1. Measure temperature directly in the water body, if possible. If not, equilibrate the sample bottle to the water's temperature, collect a sample at least 1 L in volume, and measure immediately, especially on warm days.

2. Allow the immersed thermometer to equilibrate before reading.

References

APHA, et al., Standard Methods, 17th Edition.

Smith, Craig. Personal communication, March 31, 1992.

Puget Sound Protocols, 1989.

Strong, Bernie. Personal communication, March 31, 1992.

6. CONDUCTIVITY MEASUREMENTS IN FRESH WATER

Introduction

The following procedures for operation and maintenance of conductivity instruments are based on the BECKMAN model RB-5 conductivity bridge with reference to the model RC-16C (there are 6 RB-5 and 1 RC-16C meters in the storage area). The RC-16C can simultaneously measure resistance and conductance over the range 0.2 to 2,500,000 ohms and 0.4 to 5,000,000 micromhos. The RB-5 dial indicates the sample conductivity in μmhos/cm directly over the range 0 to 1000 μmhos/cm.

The RB-5 measuring circuit is excited with 85 Hz current. The RC-16C has a two option circuit switch, 84 Hz or 1 kHz. Generally the lower frequency on the RC-16C should be used when the measured resistance is high (conductivity is low), and the higher frequency used when the measured resistance is low (conductivity is high). The RC-16C has a sensitivity control and multiplier switch which enable the meter to perform accurate and precise measurements over a greater range of conductivities than the RB-5.

Most neutral salt solutions have temperature coefficients in the order of 1/2 to 3% per degree Celsius. The conductivity increases with an increase in temperature. In order to compensate measurements for temperature, the RB-5 has a manual temperature compensator that can be set to the sample temperature, while the RC-16C measurements must be hand corrected (reference temperature section in BECKMAN RC-16C instruction manual). After setting the temperature control knob to the sample temperature, the RB-5 will provide a measure of conductivity as if the sample was being measured at the reference temperature of 25° C.

Since most of our field measurements are made with the RB-5, the following sample measurement protocol is designed for use with this instrument. If the RC-16C is used, consult the operations manual for sample measurement details.

The condition of the instrument's batteries can be checked by holding the toggle switch in the BAT CHECK position and observing the meter reading. Any reading to the right of the BAT line indicates that the batteries are good. A reading to the left of the BAT line indicates that the batteries should be replaced with standard "C" size batteries.

Conductivity Quality Control (QC) Check

Before leaving for the field, check the conductivity meter/probe(cell) against a conductivity calibration standard to make sure the readings are within the expected accuracy (± 2% of reading). Use a fresh VWR 100 μmhos/cm standard or other approved standard (one appropriate for the range that you expect to measure).

1. Soak the cell in DI water for 15-20 minutes.

   Soaking the probe breaks down the surface oxidation that occurs when the probe is not in use.

2. For performing QC checks follow procedures for sample measurement listed below by substituting conductivity standard for sample.

3. Determine the % difference between the standard and meter reading.

4. If the reading is within the expected accuracy reading (± 2 % of the meter range) the meter is okay to use. For example, with a range of 0-1000 the expected accuracy at 100 is ± 20 μmhos/cm.

Note: In low conductivity waters, the accuracy of our field instruments may not be satisfactory for quantitative use of the data (as apposed to estimating relative differences). If more accurate data are needed, water samples should be sent to the laboratory for conductivity analysis.

Sample Measurement

When measuring the conductivity of low ionic strength waters take care not to contaminate the sample. The sample container, thermometer, and conductivity cell must be thoroughly rinsed with sample prior to taking measurements. If there is a lot of dust in the air, cover the sample.

1. Before using, soak the cell in DI water for 15-20 minutes.

2. Measure the temperature of the sample within 0.5° C and set the **TEMP** dial to the measured temperature.

3. Rinse the cell at least 3 times with sample.

4. Place the cell in the sample and move it up and down in the sample a few times to make sure there are no air bubbles inside the cell.

   Before turning on the instrument, make sure the cell is immersed in the solution to a point at least 1/2" above the uppermost air vent, and should be no closer than 1/2" to the sides and bottom of the sample container.

5. Turn the instrument on by momentarily switching the toggle located in the upper right-hand corner of the control panel to the **ON** position.

   The instrument will be activated for approximately 30 seconds, then it will automatically switch off.

6. While the instrument is on, rotate the MICROMHOS/CM control knob either clockwise or counterclockwise until the meter pointer is at the null mark.

7. Record the sample conductivity from the calibrated dial as μmhos/cm.

   To obtain conductivity in standard SI units of mS/m (millisiemen/meter) or μS/m (microsiemens/meter) multiply the dial reading by 0.1 or 100, respectively. Sometimes conductivity is reported as μS/cm. In this case the values are equal (1 μS/cm = 1 μmho/cm).

8. If the meter pointer does not pass through the null position as the control knob is rotated from end to end, the conductivity of the sample may be out of the measuring range of the instrument. Since this is highly unlikely in most surface water samples, there may be a problem with the meter/cell. Reference the BECKMAN instruction manuals.

Conductivity Meter/Cell Storage

After the last measurement of the day:

1. Rinse the cell at least 3 times with DI water.

2. Clean and dry the meter/cell then replace cover.

After returning from the field:

1. If equipment problems were encountered, fill out an equipment problem report form and place it in the form holder on the file cabinet inside the electronics room. Place the defective equipment on the electronics repair bench.

2. Return meter to its proper location (it should be clean and dry!).

7. pH MEASUREMENTS IN FRESH WATER

The following procedures and tests are based on the ORION Model 250A pH meter and Triode™ pH electrode (there are 6 ORION meters with electrodes in the storage area). If the Beckman meters and electrodes are to be used, see appropriate instruction manuals for meter/electrode checks and tests. The sample measurement procedure (section IV) described in this document should be followed no matter what meter/electrode is used.

> Note: Part I and II, self test and chechout procedure only need to be performed at the beginning of each survey, not every day.

Orion Model 250A pH Meter Self-Test

1. Replace probe with BNC shorting cap.
2. Turn meter on by pressing **power** key.
3. If the battery indicator, located in the lower right corner of the display, remains on - replace the battery.
4. Press the **power** key to turn meter off.
5. Hold down the **yes** key and press the **power** key. The instrument will automatically perform an electronic and hardware diagnostic tests. If a problem is detected, the meter will display a code corresponding to the test that failed. See the trouble shooting section on page 47-51 of the instruction manual for explanation of codes.
6. After test 7, a **0** will appear on the display. Press each of the keys and the numeric digits will change (all keys must be pressed within 10 seconds or an error will be displayed).
7. The meter will then turn off then back on again.
8. If no problems are detected the meter will resume normal operations.

Meter Checkout Procedure

> Note: In order to perform the following procedure the instrument must first be cleared

of previous calibration data. This is accomplished by the following:

1. To get into setup mode, press **2nd** then **setup**.

2. Press **yes** to advance to 2-4.

3. To reset calibration data to default values press ^ key, "on" will flash, then press **yes** to reset.

1. After the self-test the meter will be in MEASURE mode indicated by the legend MEASURE on the display.

   a. Press the mode key until pH mode indicator is displayed. The main display should read a steady 7.00 ±0.02. Press **2nd cal** and when the display flashes 7.00 press **yes**.

      It takes about 10 seconds to begin flashing. When you press YES the meter pauses on either 7.00 or 7.01 then continues flashing this value.

   b. Press **measure**. The main display should read 100.0 with the legend SLP in the lower display; if so, press **yes**. If not, scroll until the display reads 100.0 then press **yes**.

      To change a value press one of the arrow keys. The first digit will flash, continue pressing the arrow key until the first digit equals the correct value then press **yes**. The second digit will flash. Again, scroll to the correct value then press **yes**. Repeat above until all digits have been changed then press **yes** again to enter the new value.

   c. The meter advances to MEASURE and the display should read a steady 7.00 or 7.01.

3. Press the mode key to enter millivolt mode. 0.0 ±0.1 should be displayed.

4. Press **mode** key to enter REL mV mode. 0.0 ±0.1 should be displayed. If not press **2nd cal** then press **yes** to enter the value 0.0. Display should read a steady 0.0.

5. After steps 1-4 have been successfully completed the meter is ready for use with an electrode. Remove the shorting plug.

Autocalibration with Two Buffers

Omit steps 1-3 if recalibrating. Use fresh 7 and 4/10 buffer solution. Buffers should bracket the expected sample range.

Prepare a solution for soaking the probe between use during the day by adding enough KCl filling solution to a volume of DI water such that the conductivity of the soaking solution is about that of the waters to be measured. Two drops of KCl filling solution in 500mL of DI water will yeild a conductivity of about 50-60 μmhos/cm. Most samplers believe soaking the probe in actual sample improves performance, however, waters with high nutrient or organic levels may foul the probe.

1. Before connecting electrode to meter check filling solution. The reference solution should be drained and refilled with fresh solution weekly (4M KCl for the ORION Triode electrodes). To replace the filler solution insert a small plastic pipet (dedicated to use only for filler solution) into the filler hole and depress the bulb. This will force the solution out of the chamber. Refill the chamber with the correct reference solution to about a 1/2" below the filler hole.

2. Connect electrode to meter. Remove storage cap from end of electrode and rinse off any salt build-up. Also, lower fill hole cover so the hole is about half open.

3. Soak the pH probe in the preprepared soaking solution for 20-30 minutes before calibration.

4. Press the **power** key and check mode arrow to make sure it is on pH. If not, press the mode key until the pH mode indicator is displayed.

5. Rinse the pH probe with DI water, then by a small amount of buffer, then place probe in pH 7 buffer. Emerse the probe such that the probe filler solution is 1/2" above the level of the sample.

   Make sure the temperature of all buffers are not above 25°C. Buffers held in the van on a hot day should be cooled down before use. It is best to have the buffer temperature close to that of the sample. See the back of buffer bottle for pH value of buffer at different temperatures.

6. Press **2nd cal**. CALIBRATION is displayed above the main field. After a few seconds P1 is displayed in the lower field which indicates the meter is ready for the first buffer.

7. When the pH value for P1 flashes, press **yes** to store the value. P2 will be displayed in the lower field indicating the meter is ready for the second buffer.

8. Rinse the probe with deionized water and then a small amount of the second buffer, then place it in the second buffer. Avoid getting any water or buffer in fill hole.

9. When the pH value for P2 flashes press **yes** to store the value.

   The meter will display the percent slope for a few seconds as a SLP (slope) message. If you miss this display, press **2nd** then **setup** and **yes** 4 times. The setup code for percent slope is 2-1 and will be displayed directly below the percent slope. The slope should fall within the range 92-102 percent.

   If the percent slope is not within this range, repeat calibration.

   If the percent slope is still not within the acceptable range reference Tracking Probe Performance section.

10 Rinse the probe with DI water and place in soaking solution.

Sample Measurement

pH is very difficult to measure with good precision and accuracy. The cold, low ionic strength waters of Washington are particularly difficult to measure. Temperature can affect the electrode potential and change the hydrogen ion activity within a sample (both cause pH drift) while low conductivity can cause liquid junction error and pH drift. The electrode potential problem due to temperature can be mitigated by allowing the electrode to come to the same temperature as the sample. Although the meter/electrode is temperature compensated it cannot compensate for potential differences due to the probe/solution temperature differences. Addressing changes in hydrogen ion activity is a little more difficult, because the sample usually changes temperature as the measurement is being taken, especially on a warm day. Taking a large volume of sample or holding a smaller container in the waterbody to be measured will help maintain a constant temperature in the sample and minimize pH drift. Addressing the low ionic strength problem is much more difficult.

Ideally, in low ionic strength waters it would be best to take a pH measurement quickly to avoid CO_2 changes in the sample, but the combination of temperature effects on the electrode and liquid junction error requires approximately 2-3 minutes equilibration time to mitigate. In this time, there can be additional pH drift caused by chemical changes. There is NO simple answer

to this additional problem, however, it is expected to be relatively small for surface water samples.

The best solution to all of the problems mentioned above is to maintain a consistent approach in measuring pH so that measurements are comparable between sites, surveys, and projects. To address these problems we recommend waiting two minutes, then take the first reading after the READY indicator is displayed on the screen. At this point, if the sample temperature is constant, the rate of drift due to temperature affects on the electrode and junction error should be minimized. The following pH sample measurement procedure is designed to address the problems mentioned above and provide consistency in pH measurements.

1. Rinse sample container with sample.

   If you will be taking the sample back to the van for measurement, collect it in a clean bucket. If measurement to be performed at the waterbody, use plastic container that can be held in the water.

2. Remove the probe from the soaking solution and rinse with sample before placing it in the sample. Make sure vent hole is about half uncovered.

   Shake the probe in the sample to make sure there are no air bubbles caught next to the bulb (air bubbles trapped next to the sensors will also cause drift). Emerse the probe such that the probe filler solution is about 1/2" above the level of the sample.

3. Press the **power** key on the meter. Make sure the mode arrow is pointing at pH.

4. Wait 2 minutes, then when the ready function has locked on (located in the right center of the display) record the pH measurement to the nearest 0.01 pH units. Values should be rounded for reports by the project officer to the nearest 0.1 pH unit. For the first measurement of the day, soaking the probe in the sample for 4-5 minutes without the meter on may improve the response time.

5. Place the probe back in the soaking solution.

It makes little difference whether your sample is stirred or static as long as your method is consistent (The Beckman Handbook of Applied Eclectrochemistry). In order to minimize noise, potential shifts, and chemical changes in the sample and to maintain consistency, we recommend NOT stirring the sample.

pH Quality Control Check

Check the pH meter/probe with the 6.97 low ionic strength buffer three times a day. Immediately after initial calibration, at the midway point of the sampling day and after the last sample of the day. If the pH is not within 0.1 of the true pH, recalibrate the meter. If the meter fails again, reference the troubleshooting section of the meter and probe instruction manuals. If there is a problem, it is probably the probe. The following section describes indicators of probe reliability.

Tracking Probe Performance

As mentioned, if the percent slope does not fall within the range 92 - 102 there may be a problem with the electrode. If the % slope is outside this range perform the following check.

1. Calibrate the pH meter to pH 7 and pH 4/10 (see Calibration and Standardization).

2. Place the pH probe in 7 buffer.

3. Press the **mode** button until the mode arrow aligns with mV (millivolts).

4. Press the **measure** button on the pH meter and record the value.

5. Repeat step 4 for the other pH buffer used in the two point calibration.

6. Compare the mV measurement in 4 and 5 above to the acceptable ranges.

   Within $\pm$30 mV at pH 7 and the difference between mV measured at pH 4/10 and pH 7 should be 160 - 180 mV.

7. If mV readings are outside the specified ranges, drain and refill with fresh filling solution. Repeat steps 1 - 6.

8. If mV readings are within the ranges, but electrode response is slow or drifting badly, drain and refill with fresh filling solution.

9. If replacing the filling solution does not correct the problem; replace the electrode and fill out an equipment problem report form (see section VII)

pH Meter/Probe Storage

After the last measurement of the day:

1. Rinse the probe with DI water.

2. Place a few drops of storage solution in the protective cap and cover the sensing elements.

3. Cover the fill hole with the protective sleeve.

After returning from the field:

1. If equipment problems were encountered, fill out an equipment problem report form and place it in the form holder on the file cabinet inside the electronics room. Place the defective equipment on the electronics repair bench.

2. Return all pH equipment to its proper location (it should be clean and dry!).

When to Change the pH Probe

If general maintenance & cleaning procedures fail to correct measurement problems, the probe should be replaced if any of the following conditions exist:

1. The probe exceeds the manufacturer's recommended life expectancy of 18 months.

2. Offset is >30 mV in pH 7 buffer or the difference between pH 7 and 4/10 is >160 to 180 mV.

3. Slope is outside the 92-102%.

4. The probe fails the pH quality control check on two successive tries.

8. DISSOLVED OXYGEN DETERMINATION: AZIDE-MODIFIED WINKLER TITRATION

Introduction

Dissolved Oxygen (DO) is frequently determined by using the azide-modified Winkler titration method. Samples are collected and preserved in the field, and titrated upon return using the setup in the boatshed. The Winkler method is preferred over the electrode membrane method for general field monitoring because of its ease and low cost, and because of the difficulty encountered in maintaining oxygen-meter calibration. The membrane electrode method is preferred for obtaining depth profiles in lakes and rivers.

The azide modification is employed because it effectively removes interferences caused by nitrite. Other modifications of the Winkler method are used when samples contain other interferences such as: ferrous iron; ferric iron salts; biological flocs (activated sludge); and samples high in total suspended solids. Sampling for DO requires care, since contact between the sample and the air may modify the results.

Before Sampling

The DO lab at the boatshed is maintained by "everybody." Please do your part to keep it clean, tidy and safe. Titration chemicals and equipment are maintained by the Ambient Monitoring Section (AMS). Bottles and preservatives for each van, or for each project are maintained by the van custodian and/or project officer.

The project officer should contact AMS (Brad Hopkins) several months before samples are to be collected so that adequate supplies of chemicals can be ordered and that conflicts between scheduled maintenance and titration needs can be avoided. The project officer should check all equipment and reagents before sampling and notify others involved in the project of the status of the DO lab and other equipment. The project officer is also responsible to coordinate with AMS (Brad Hopkins) for the replacement/repair of DO equipment and/or chemicals.

The following procedures were compiled from a variety of references including the personal experiences of EILS personnel.

Containers

300 ML glass biological oxygen demand (BOD) bottles, narrow and flared mouth, tapered and pointed ground glass stoppers.

Containers should be cleaned as needed with soap and water and well rinsed with tap water. If the DO bottles are used with the metal bucket bridge sampler and will come in contact with water to be used for nutrient samples, they should be acid cleaned to lessen the risk of contaminating the nutrient sample. To acid clean: soak for 24 hours in 10% HCl solution, rinse 3 times with deionized water, and air dry.

Store bottles upside down on a perforated mat to promote drying and to keep out dust. Store glass stoppers in a manner that prevents dust and other contaminants from adhering to them.

Check DO bottle numbers before sampling to ensure that all numbers are different (no duplications) to avoid sample confusion.

Sample Collection

Sample collection techniques will vary depending upon the situation and the sampling apparatus used. Most commonly used apparatus includes: Kemmerer sampler, stainless steel sampling bucket, and, a polyethylene (PE) bottle with tube attached. Each of these require specific techniques in order to collect a "good" sample. Filling the DO bottle directly is <u>not</u> recommended because of the likelyhood of turbulent filling and/or sampling of the water's surface film.

A. Prepare to Sample

1. Ensure that sample bottles and transfer apparatus are clean.

2. Temperature of the water needs to be determined and recorded at the same time the sample is taken.

3. Atmospheric pressure and/or station altitude need to be determined and recorded.

B. Collect the sample

1. Rinse bottle and stopper with sample (2-3 times) before filling.

2. Collect sample just under the surface and in the upper 1/2 meter of the water body (unless collecting at predetermined depths). Avoid collecting the surface film. Avoid entraining or dissolving atmospheric oxygen. Prevent turbulence and bubble formation. With the Kemmerer and PE bottle with tube, insert tube to bottom of DO bottle and allow bottle to fill. Avoid air that may pass through tube into DO sample. Allow DO bottle to overflow for approximately 10 seconds or by two to three volumes. Avoid agitation of sample. With the Kemmerer, do not allow a "suction" on the sample to form as it is transferred to the DO bottle - ensure that the sampler is vented before draining it.

C. Stopper the Sample

1. Ensure that no air bubbles remain in bottle after filling. If bubbles adhere to the sides of the bottle, dislodge them by tapping bottle with the top part of the glass stopper. If bubbles prove difficult to remove, collect another sample and/or use another bottle (bubble trapping bottles probably need cleaning).

2. Stopper immediately. Don't let sample remain in contact with air after collection. Avoid trapping air as the stopper is inserted.

3. Once stoppered, dump the excess sample from the top of the bottle. This ensures that the sample volume used to determine DO is correct; adding preservatives to an unstoppered and full-to-the-lip bottle may result in over-estimating the DO content of the sample.

Preservation

References indicate that sample preservation include addition of three preservatives after the sample is collected (manganous sulfate, alkali-iodide-azide, and sulfuric acid). We deviate from this by adding the acid just prior to titration rather than adding acid to the freshly collected sample. As such, we need to transport and handle only two preservatives in the field.

Samples that have an appreciable oxygen or iodine demand should have DO determined immediately. (Iodine demand occurs in waters experiencing intense phytoplankton growth - see references for preservation of, and subsequent correction for, iodine demanding samples).

A. Prepare Preservatives and Dispensers

1. Ensure that preservatives are fresh and that the dispensing equipment is clean. Small, plastic, bulb-type pipets are commonly used. Automatic pipets have not worked well due to infrequent use and difficulty of maintenance. The alkali-iodide-azide solution spoils easily. This supersaturated solution will form precipitate with the introduction of dirt or other impurities and be difficult to pipet.

2. Transport only small amounts of the preservatives into the field. 125 mL brown PE bottles (usually used for ortho-phosphate samples) are commonly used to transport preservatives. Only 2 mL of each preservative is needed per sample.

3. Label reagents and pipets to avoid cross contaminaiton. Have extra pipets on hand. Store pipets in a manner that will prevent their coming into contact with contaminants (e.g. bucket bottoms, van drawers, etc.).

B. Preserve the Sample

1. Remove stopper from bottle (holding the upper, flat part between fingers with stopper pointing away from the back of your hand works for many people), avoid agitating the sample.

2. Add 2 mL manganous sulfate to the sample first. (NOTE: The order that preservatives are added is critical). Hold pipet tip just above the surface of the sample and dispense reagent. Avoid introducing air into the sample. Do not submerge the tip of the dispenser into the sample, air might inadvertently be introduced into the sample. If the pipet is dipped into the sample, discard the pipet to prevent contamination of the reagent stock.

3. Add 2 mL alkali-iodide-azide solution to the sample in the same manner as the manganous sulfate (avoid contact with skin). A brown precipitate will begin to form. Samples with very low DO may exhibit a milky-white floc.

   (Standard Methods 16th Ed. states to add 1 mL, rather than 2 mL, of each of the two fixing reagents. We add the reagents to "excess," and this is accounted for during the transfer of prepared sample to the titrating flask; the volume used is 203 mL rather than 201 mL)

4. Inspect the bottle for the presence of air bubbles entrained during the fixing process.

If needed, dislodge bubbles by tapping the bottle with the glass stopper.

5. Stopper carefully to exclude air and twist stopper gently to ensure a good seal. Mix sample by inverting the bottle several times. The brown precipitate will begin to settle. Rinse bottle of chemical residue with stream water or DI.

6. Add DI or stream water to bottle/stopper top to provide a water seal. Cap bottle with plastic cap to prevent water seal from evaporating or spilling. Record sample bottle number, time, location, etc.

C. Store the Sample

Store samples in the dark and at the temperature of the water source or at 10-20 degrees Celsius. Samples should be titrated as soon as possible. For iodine or oxygen demanding samples, see APHA 1985 and/or 1989.

(Most references state that samples should be titrated within a few hours or within 8 hours - this is coincident with field acidification of the sample as well. Our practices vary and samples have been stored for several days with 2 preservatives before adding acid and titrating. We recommend titrating as soon as possible, at the end of the day (within 8 hours). If samples are held longer before titrating, remarks indicating the longer holding time should be made in the methods section of the report).

Titration

A. Gather and Check Equipment:

1. Ensure there is enough 0.025 N sodium thiosulfate to titrate your samples. Loosen the top of the resevoir to allow for free flow of this reagent. If the top was already loose, make a note of it. If reagent needs to be added from the stock in the refrigerator, we recommend delaying titrations until the cold reagent equilibrates to room temperature.

2. Check the buret to be sure that some reagent has been left in the lower portion. Reagent should be present to about an inch above the 3-way stopcock. If it isn't, or is below the stopcock, ensure that no air is trapped in the assembly.

   If air is present, it must be removed because it may cause errors in volume

measurements. Some techniques: (a) flush out air by quick opening of the stopcock; (b) carefully turn buret on its side and open the stopcock to help air bubbles travel down the buret tip. Be careful of where the reagent is draining during these operations; (c) fill a small red squeeze bulb (from the old automatic pipettors) with sodium thiosulfate and then hold this over the tip of the buret, open the stopcock for the buret (not the reservoir), and squeeze the bulb to force reagent into the buret resulting in air being pushed out the top of the buret. After clearing air, check for proper operation.

3. If no air is present, then fill the buret nearly full. Orient yourself to the operation of the 3-way stopcock. Then flush "stale" reagent from the lower tip of the buret. Alternatively, lower and raise the reagent reservoir to allow reagent in the buret and lines to mix with the reservoir contents. Do this several times. Refill the buret until reagent escapes from the top nipple. The buret is now ready for titration.

B. Acidify and Prepare the Sample for Titration

Sample preparation involves acidifying the sample and measuring out the precise volume to be titrated. Most people acidify all the samples before proceeding to titrate them, or if working as a team, one person acidifies while the other titrates the samples. It is important to titrate as soon as possible after acidifying because the sample is now photosensitive. (How soon is ASAP? Who knows? Common practice seems to produce a titration within an hour of acidification. Some titrators prefer to titrate immediately after acidifying).

1. Remove plastic caps from the bottles. Invert bottle several times to mix the floc. Allow floc to settle until the upper half of the bottle is clear. Bubbles may be present just under the stopper; this is likely nitrogen that off-gassed due to the sample source being supersaturated.

2. Remove stopper and add 2 mL of concentrated sulfuric acid. CAUTION: hydrogen sulfide gas may be produced in samples that contain low DO.

3. Replace stopper. Rinse stoppered bottle tops with tap water and then mix sample by inverting bottle several times. The floc should dissolve and the sample take on an amber color.

   If not all of the floc dissolves (as with some supersaturated samples) add just enough acid to dissolve the remaining floc; add a bit - mix - observe - add more if necessary. Return the acid dispenser to the acid storage cabinet immediately after acidifying all samples.

4. Obtain a clean 500 mL Erlenmeyer flask, magnetic stir bar, and a 203 mL plastic volumetric flask. Rinse each with tap water before proceeding. The Erlenmeyer flask should be thoroughly rinsed (3 times) with tap water between samples. Do not rinse the Erlenmeyer flask with the sample to be titrated, rinse with water only.

5. Rinse the volumetric flask 3 times with the acidified sample. Do not rinse the volumetric flask with water between samples, rinse only with the sample to be transferred.

6. Fill the volumetric flask with the acidified sample. Before filling, check the rubber collar at the top of the flask to be sure that it doesn't extend above the cut portion of the flask (this would result in error of measurement).

7. Transfer the measured sample from the volumetric flask to the Erlenmeyer flask without spilling or losing any. A magnetic stir bar should be in the flask. The sample is ready for titrating. Make note of the DO bottle number.

C. Titrate the Sample

1. Ensure that the sodium thiosulfate buret is full. Place flask with sample on the magnetic stir plate under the buret, magnetic stirrer should be on and the sample swirling.

2. Add sodium thiosulfate from the buret, continue titrating until the sample turns a pale straw color. Slow the addition of sodium thiosulfate as you approach this pale straw color. Titrate as close to a clear color as you can without turning the sample clear; this should be within about 1 mL addition of titrant from the endpoint (the endpoint being when the sample turns clear).

3. Add 1-2 mL (several drops) of starch directly to the sample. The sample will turn a cobalt blue color yet should remain transparent. Avoid adding starch to the sides of the flask. Addition of too much starch may make the endpoint difficult to determine or "mushy"; the color will be an opaque blue or even appear black. Addition of starch too early in the titrating process may also make the endpoint "mushy." Bad starch may also make the endpoint mushy. Mentally note the volume of titrant added as you approach the endpoint.

4. Continue titrating slowly (drop by drop) until the blue color just disappears and the sample turns clear. This is the endpoint.

5. Record the volume of titrant added to the nearest 5/100th mL. The mLs of titrant needed to reach the endpoint is equivalent to the DO content of the sample in mg/L, however, a correction factor may need to be applied (see Standardization below).

D. Back-titrating

If the endpoint is overrun (addition of titrant after the sample turns clear), a correction can be made only if the endpoint is overrun by no more than 6-8 drops of titrant (0.3-0.4 mL).

1. Record the volume of titrant used.

2. Backtitrate with the bi-iodate standard (use the small bottle with the eyedropper) by adding one drop at a time to the clear sample. Count the number of drops until the sample turns a blue color. Add no more.

3. Multiply the number of drops by 0.05 (each drop of backtitrant is 0.05 mL volume) and subtract this product from the amount of titrant used. The result is the volume of titrant (sodium thiosulfate) used to obtain the endpoint of the sample.

This "backtitrate" process can only be performed once on a sample. Disregard subsequent recolorations due to the catalytic effect of nitrate or to traces of ferric salts that have not been complexed with fluoride. Another option is to re-titrate a 50 mL sample taken from the remaining sample in the DO bottle. Measure 50 mL with a graduated cylinder, transfer to a clean Erlenmeyer flask, and titrate. Correction factor is as follows:

(mL titrant) X (203/50) = mg/L DO.

E. Standardize the Sodium Thiosulfate Solution

Standardization of the sodium thiosulfate solution is required to ascertain the condition of this relatively unstable reagent. Standardize the titrant at the beginning and end of a set of samples (first and last samples). With large sample sets (>25 samples) you may wish to perform a third standardization in the middle portion of the titrating session.

After the first sample is titrated to its end point, add 10.00 mL of the bi-iodate standard to the sample and retitrate until the endpoint is reached. Record the volume of sodium thiosulfate needed to retitrate. (Also record this on the sheet kept near the titrating equipment for reference by AMS.) Repeat this procedure on one of the final samples of the set.

To add 10.00 mL bi-iodate standard to the sample, use the apparatus set up at the titrating bench. This apparatus involves a volumetric pipet semi-permanently attached to the bi-iodate standard container. We recommend that you practice with and learn to use this apparatus before titrating so that precise volume measurements will be made. Do not use a pipet and squeeze bulb to extract and dispense bi-iodate standard because of potential contamination of the bi-iodate standard.

The correction factor (CF) is developed from this standardization procedure as follows:

CF = 10.00 mL bi-iodate/mLs of sodium thiosulfate used in re-titration

Multiply each sample titration result by this factor to get the DO of the sample. If the first and last (and middle) standardization checks result in different correction factors, apply the correction factors using your best judgement.

"Gear Down" and Clean Up After Yourself

After completing your titrations, please clean up and secure all equipment.

1. Drain the sodium thiosulfate buret to within an inch of the stopcock.

2. Close the lid on the resevoir by gently tightening it.

3. Tighten the lid on the bi-iodate container.

4. Ensure that the sulfuric acid is put away in the acid storage cabinet.

5. Rinse all glassware used and put on the drying rack. DO bottles, stoppers and plastic caps usually go back to the van from which they came.

Please notify AMS (Brad Hopkins) and the project officer about any equipment or chemical stock concerns (e.g., broken glassware, bad starch, low supply of sulfuric acid, etc.).

Calculations

See APHA 1980, 1985 and/or 1989 for correction procedures for saline samples and percent saturation calculations at various barometric pressures.

Spreadsheets that perform these calculations may exist among some WAS staff.

QA/QC

The QA/QC program and procedures are the responsibility of the project officer. The whole DO determination system should be considered. This involves titrating apparatus and chemicals, field replication and lab replication.

Check with AMS (Brad Hopkins) prior to sampling about the condition of the apparatus and chemicals. Condition of the preservatives used in the field need to be evaluated.

Field replication at 10-15% of total sample size is usually adequate and most commonly performed as part of QA/QC. Other considerations:

(a) Puget Sound Protocols (PSP, 1990) recommends randomly selecting 5-10% of samples for field duplication and 5-10% for duplicate laboratory analysis. (We usually don't do lab replicates because the bottle doesn't contain enough sample for two titrations).

(b) PSP recommends running one calibration sample per batch of samples. This calibration sample would come from an aerated tank of clean water that is at 100% saturation. Such a tank is located in the boatshed.

If samples are expected to contain low DO concentrations, then a zero calibration standard is recommended. There are several methods to prepare such a solution, consult APHA 1985/1989. APHA (Standard Methods) also contains tables that aid in determining DO concentrations at different temperatures and pressures.

Data Confidence

Precision, expressed as a standard deviation, of this method is about 0.02 mg/L with distilled water and about 0.06 mg/L in wastewater and secondary effluent. In the presence of appreciable interferences, the standard deviation may be as high as 0.10 mg/L. Greater

errors may occur in waters having organic suspended solids or heavy pollution.

DO results are commonly reported to the nearest 0.10 mg/L. Consistency in the method used to round numbers is recommended. Various methods are employed in evaluating replicate analyses, so the method used should be stated in the report.

References

APHA Standard Methods, 15th (1980), 16th (1985) and 17th (1989) Editions.

Puget Sound Protocols, 1990. Freshwater Protocols Chapter.

EILS memos by Brad Hopkins (3/13/89) and Nicky Rushing (7/23/90).

ASTM Technical Publication No. 148-1 (collection equip. and technique).

USGS Water Supply Paper No. 1454 (collection equip. and technique).

Recommended procedures for the azide-modified Winkler method are:
APHA (1985) Standard Methods, Method 421B
US EPA (1983) Method 360.2

9. DO DETERMINATIONS WITH THE YSI 57 DISSOLVED OXYGEN METER

Introduction

The YSI Model 57 Dissolved Oxygen Meter is intended for dissolved oxygen and temperature measurement in water and wastewater applications, but is also suitable for use in certain other liquids. Dissolved Oxygen is indicated in mg/L (milligrams per liter) on 0-5, 0-10 and 0-20 mg/L scales. Temperature is indicated in degrees C on a -5 to +45 C scale. The dissolved oxygen ranges are automatically temperature compensated for solubility of oxygen in water and permeability of the probe membrane; salinity is manually compensated.

The probes use Clark-type membrane covered polarographic sensors with built in thermistors for temperature measurement and compensation. A thin, permeable membrane stretched over the sensor isolates the sensor elements from the environment, but allows oxygen and certain other gases to enter. When a polarizing voltage is applied across the sensor, oxygen that has passed through the membrane reacts at the cathode, causing a current to flow.

The membrane passes oxygen at a rate proportional to the pressure difference across it. Since oxygen is rapidly consumed at the cathode, it can be assumed that the oxygen pressure inside the membrane is zero, hence, the force causing the oxygen to diffuse through the membrane is proportional to the absolute pressure of oxygen outside the membrane. If the oxygen pressure increases, more oxygen diffuses through the membrane and more current flows through the sensor, a lower pressure results in less current.

Our meters generally use the YSI 5739 Probe. Check the probe model before using, and for other probes, see manufacturer's instruction manual.

Preparing the Probe:

All YSI 5700 Series Probes have similar sensors and should be cared for in the same manner. They are precision devices relying on good treatment. In order to make accurate measurements, the probe should be prepared as follows:

Note: For new probes, see manufacturer's instructions that accompany the probe.

1. If needed, prepare electrolyte by dissolving the KCl crystals in the dropper bottle with distilled water (provided by manufacturer). Fill the bottle to the top. KCl solution

that is older than 60 days should be replaced. Replacement solution should meet manufacturer's requirements.

2. Unscrew the sensor guard from the probe (YSI 5739 only) and then remove the "O" ring and membrane. Thoroughly rinse the sensor with KCl solution.

3. Fill the probe with electrolyte as follows:

   A. Grasp the probe in your left hand. When preparing the YSI 5739 probe, the pressure compensating vent should be to the right. Successively fill the sensor body with electrolyte while pumping the diaphragm with the eraser end of a pencil or similar soft, blunt tool. Continue filling and pumping until no more air bubbles appear. (With practice, you can hold the probe and pump with one hand while filling with the other).

   B. Secure a membrane under your left thumb, then add more electrolyte to the probe until a large meniscus completely covers the gold cathode.

   Note: Handle membrane material with care, keeping it clean and dust free, touching it only at the ends.

   C. With the thumb and forefinger of your other hand, grasp the free end of the membrane.

   D. Using a continuous motion stretch the membrane UP, OVER, and DOWN the other side of the sensor, this stretching forms the membrane to the contour of the probe.

   E. Secure the end of the membrane under the forefinger of the hand holding the probe.

   F. Roll the "O" ring over the end of the probe. There should be no wrinkles in the membrane or trapped air bubbles. Some wrinkles may be removed by lightly tugging on the edges of the membrane beyond the "O" ring.

   G. Trim off excess membrane with scissors or sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.

4. Shake off excess KCl and reinstall the sensor guard.

5. A bottomless plastic bottle is provided with the YSI 5739 probe for convenient storage, place a small piece of moist towel or sponge in the bottle and insert the probe into the open end. This keeps the electrolyte from drying out.

Probe Storage:

Proper probe storage is essential for optimum performance and extension of probe life.

For short term storage (less than 3 weeks), the probe may be stored in the operation ready state. Moisten the paper or sponge at the bottom of the probe storage bottle and insert the probe. The moist environment prevents electrolyte from evaporating and the membrane from drying out. Do not store membrane in water; algal and bacterial growth may occur on the membrane and affect probe performance.

For long term storage (greater than 3 weeks), the probe is stored dry, without electrolyte. Remove the membrane, flush out the electrolyte with deionized water, blow most of the water out with low pressure air (a pursed-lip blow should suffice), install a new membrane (not necessary to trim excess), replace protective cap, remove moist towel or sponge from storage bottle and cover probe with the dry storage bottle. Tag the meter or probe with the statement DRY STORAGE, date and initial the tag. For longer periods of time, dry storage lengthens probe life by decreasing the dissolving of silver (anode) into the electrolyte (and subsequent deposition on the gold cathode).

Membrane Information:

Membranes will last indefinitely, depending on usage. Average replacement is 2-4 weeks, however should the electrolyte be allowed to evaporate and an excessive amount of bubbles form under the membrane, or the membrane becomes damaged, thoroughly flush the reservoir with KCl and install a new membrane. Also replace the membrane if erratic readings are observed or calibration is not stable.

High Sensitivity Membrane:

Although we most commonly use the standard .001" (YSI 5775) membrane, .0005" high sensitivity membranes are available. Use a high sensitivity .0005" membrane (YSI 5776) in place of the standard .001" membranes (YSI 5775) when measurements are to be made consistently at low temperatures (less than 15 C) or low DO levels. Calibration and readings are made just as if the standard YSI 5775 membrane was being used.

Probe Performance:

The gold cathode should always be bright and untarnished. To clean, wipe with a clean lint-free cloth or hard paper. NEVER USE ANY FORM OF ABRASIVE OR CHEMICAL. Rinse the sensor several times with KCl, refill, and install a new membrane.

The YSI Technical Representative does approve using a very fine emery paper or ink pen eraser to polish the gold cathode. Great care is needed however, because the gold plating layer is very thin, excessive polishing may result in the need for cathode replating.

Use of the YSI 5680 Probe Reconditioning Kit may be used to help remove accumulated tarnish and silver deposits from the gold cathode while maintaining the spherical contour of the probe face.

Some gases can contaminate the sensor, evidenced by discoloration of the gold cathode and silver anode. Repeated exposure to hydrogen sulfide or sulfur dioxide, in particular, will tarnish the electrode. The silver anode of a new probe can vary in color from a pearly white to medium grey. As it tarnishes it will get darker in color. "Poisoning" of the anode can cause loss of sensitivity and the inability to calibrate the system.

A tarnished silver anode can usually be rejuvenated by removing the membrane and soaking the probe in a 14% solution of ammonium hydroxide for 2 to 3 minutes. Longer soaking in this concentrated solution may damage the probe. An alternative is to soak the probe in a 3% ammonium hydroxide solution overnight. After treatment, thoroughly flush the probe with deionized water and prepare for use. If these reconditioning procedures do not restore probe performance, return the probe to YSI Product Services for restoration.

H_2S, SO_2, halogens, neon, nitrous and nitric oxide, chlorine and CO are interfering gases. If you suspect erroneous readings, it may be necessary to determine if these are the cause. See manufacturer's instruction manual for gases that have been tested for response.

If the probe has been operated for extended periods with a loose or wrinkled membrane, the gold cathode may become plated with silver. In this event, return the probe to the factory for refinishing.

Preparing the Instrument:

It is important that the instrument be placed in the intended operating position: vertical, tilted, or on its back - before it is prepared for use and calibrated. Readjustment may be necessary when the instrument operating position is changed.

After preparing the probe, proceed as follows:

1. With switch in the OFF position, adjust the meter pointer to zero with the screw in the center of the meter panel. Readjustment may be necessary if the instrument position is changed.

   However, YSI Technical Representative states that as long as strong shocks and instrument jarring or movement are avoided, readjustment may not be needed. The concern with moving the instrument is the upsetting or movement of the calibration dials and/or a shock strong enough to alter the mechanical zero of the needle.

2. Switch to RED LINE and adjust the RED LINE knob until the meter needle aligns with the red mark at the 31 C position.

3. Switch to ZERO and adjust to zero with zero control knob.

4. Attach the prepared probe to the PROBE connector of the instrument and adjust the retaining ring finger tight.

5. Before calibrating allow 15 minutes for optimum probe stabilization. Repolarize whenever the instrument has been OFF or the probe has been disconnected.

Calibration

The operator has a choice of three calibration methods - Winkler Titration, Saturated Water, and Air. Air calibration is quite reliable, and far simpler than the other two methods. Ensure that no air bubbles are present in the electrode (the instrument "reads" air bubbles as an oxygen saturated sample). The three methods are described in the following paragraphs.

Air Calibration:

1. Place the probe in moist air. BOD probes can be placed in partially filled (50 mL) BOD bottles. Other probes can be placed in the YSI 5075A Calibration Chamber

(refer to the following section describing calibration chamber) or the small storage bottle (the one with the hole in the bottom) along with a few drops of water. The probe can also be wrapped loosely in a damp cloth taking care the cloth does not touch the membrane. Shake any droplets of water off of the probe surface to prevent a cooling effect. Wait approximately 15 minutes for temperature stabilization.

2. Switch to TEMPERATURE and read. Refer to Table I - "Solubility of Oxygen In Fresh Water" and determine calibration value.

3. Determine altitude or atmospheric correction factor from Table II.

4. Multiply the calibration value from Table I by the correction factor from Table II.

   EXAMPLE: Assume temperature = 21°C and altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/L. From Table II, the correction factor for 1000 feet is about 0.96. Therefore, the corrected calibration value is 8.9 mg/L X 0.96 = 8.54 mg/L.

5. Switch to the appropriate mg/L range, set the SALINITY knob to zero and adjust the CALIBRATE knob until the meter reads the correct calibration value from Step 4. Wait two minutes to verify calibration stability. Readjust if necessary.

The probe is now calibrated and should hold this calibration value for many measurements. Calibration can be disturbed by physical shock, touching the membrane, turning the instrument off, or drying out of the electrolyte. Check calibration after each series of measurements and in time you will develop a realistic schedule for recalibration.

Table I shows the amount of oxygen in mg/L that is dissolved in air saturated fresh water at sea level (760 mmHg atmospheric pressure) as temperature varies from 0 to 45 C.

Table I - Solubility of Oxygen in Fresh Water

Temperature Degrees C	mg/L Dissolved Oxygen	Temperature Degrees C	mg/L Dissolved Oxygen
0	14.60	23	8.56
1	14.10	24	8.40
2	13.81	25	8.24
3	13.44	26	8.09
4	13.09	27	7.95
5	12.75	28	7.81
6	12.43	29	7.67
7	12.12	30	7.54
8	11.83	31	7.41
9	11.55	32	7.28
10	11.27	33	7.16
11	11.01	34	7.05
12	10.76	35	6.93
13	10.52	36	6.82
14	10.29	37	6.71
15	10.07	38	6.61
16	9.85	39	6.51
17	9.65	40	6.41
18	9.45	41	6.31
19	9.26	42	6.22
20	9.07	43	6.13
21	8.90	44	6.04
22	8.72	45	5.95

Source: Derived from 15th Edition "Standard Methods for the Examination of Water and Wastewater."

Table II shows the correction factor that should be used to correct the calibration value for the effects of atmospheric pressure or altitude. Find true atmospheric pressure in the left hand column and read across to the right hand column to determine the correction factor. (Note that "true" atmospheric pressure is as read on a barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level). If atmospheric pressure is unknown, the local altitude may be substituted. Select the altitude in the center column and read across to the right hand column for the correction factor.

Table II - Altitude Correction Factors

Atmospheric Pressure mmHg	or	Equivalent Altitude Feet	=	Correction Factor
775		-540		1.02
760		0		1.00
745		542		.98
730		1094		.96
714		1688		.94
699		2274		.92
684		2864		.90
669		3466		.88
654		4082		.86
638		4756		.84
623		5403		.82
608		6065		.80
593		6744		.78
578		7440		.76
562		8204		.74
547		8939		.72
532		9694		.70
517		10472		.68
502		11273		.66

Source: Derived from 15th Edition "Standard Methods for the Examination of Water and Wastewater"

Winkler Titration:

1. Draw a volume of water from a common source and carefully divide into four samples. Determine the oxygen in three samples using the Winkler Titration technique and average the three values. If one of the values differs from the other 2 by more than 0.5 mg/L, discard that value and average the remaining two.

2. Place the probe in the fourth sample and stir.

3 Set the SALINITY control to zero or the appropriate salinity value of the sample.

4. Switch to desired mg/L range and adjust the CALIBRATION control to the average value determined in Step 1. Allow the probe to remain in the sample for at least two minutes before setting the calibration value, and leave in the sample for an additional two minutes to verify stability. Readjust if necessary.

Saturated Water:

1. Air saturate a volume of water (300-500cc) by aerating or stirring for at least 15 minutes at a relatively constant temperature.

2. Place the probe in the sample and stir. Switch to TEMPERATURE. Refer to Calibration Table I for the mg/L value corresponding to the temperature.

3. Determine local altitude or the "true" atmospheric pressure (note that "true" atmospheric pressure is as read on a mercury barometer. Weather Bureau reporting of atmospheric pressure is corrected to sea level). Using Table II determine the correct factor for your pressure or altitude.

4. Multiply the mg/L value from Table I by the correction factor from Table II to determine the corrected calibration value for your conditions.

   EXAMPLE: Assume temperature = 21°C and altitude = 1000 feet. From Table I the calibration value for 21°C is 8.9 mg/L. From Table II the correction factor for 1000 feet is about 0.96. The corrected calibration value is 8.9 mg/L X 0.96 = 8.54 mg/L.

5. Switch to an appropriate mg/L range. Set the SALINITY knob to zero, and adjust the CALIBRATE knob while stirring until the meter reads the corrected calibration value from Step 4. Leave the probe in the sample for two minutes to verify calibration stability. Readjust if necessary.

Dissolved Oxygen Measurements

With the probe prepared for use and the instrument calibrated, place the probe in the sample to be measured and provide stirring.

1. Adjust the SALINITY knob to the salinity of the sample.

2. Provide manual stirring by raising and lowering the probe about 1 feet per second or "stir" the probe (horizontally) in the sample container. Maintain a horizontal stirring rate of about 1 foot per second.

   Stirring for the 5739 Probe can best be accomplished with a YSI submersible stirrer, just turn the STIRRER knob ON.

3. Allow sufficient time for the probe to stabilize to sample temperature and dissolved oxygen. A time of 30 seconds is usually sufficient for the temperature and DO reading to stabilize. If DO readings appear jumpy or seem to fall off, inadequate or inconsistent stirring may be the cause. Read dissolved oxygen only when the temperature and DO readings have stabilized.

Measurment Errors

There are three basic types of errors which can occur. Type I errors are related to limitations of the instrument design and tolerances of the instrument components. These are chiefly the meter linearity and resistor tolerances. Type II errors are due to basic probe accuracy tolerances, chiefly background signal, probe linearity, and variations in membrane temperature coefficient. Type III errors are related to the operator's ability to determine the conditions at the time of calibration. If calibration is performed against more accurately known conditions, Type III errors are appropriately reduced.

See manufacturer's instruction manual for discussion of errors and an example of an error calculation.

Specifications

I. Instrument

Oxygen Measurement

Ranges: 0-5, 0-10 and 0-20 mg/L (0-2, 5, 0-5 and 0-10 mg/L with YSI 5776 High Sensitivity Membrane)

Accuracy: ±1% of full scale at calibration temperature(±0.1 mg/L on 0-10 scale), or 0.1 mg/L (whichever is larger)

Readability: 0.025 mg/L on 0-5 scale 0.05 mg/L on 0-10 scale; 0.1 mg/L on 0-20 scale

Temperature Measurement

Range: -5 to +45°C

Accuracy: ±0.5°C plus probe which is ±0.1°C

Readability: 0.25°C

Temperature Compensation

±1% of DO reading for measurements made within ±5°C of calibration temperature.

±3% of D0 reading over entire range of -5 to +45°C probe temperature.

System Response Time

Typical response for temperature and DO readings is 90% in 10 seconds at a constant temperature of 30°C with YSI 5775 membranes. DO response at low temperature and low DO, is typically 90% in 30 seconds. YSI 5776 High Sensitivity Membranes can be used to improve response at low temperature and low DO concentrations. If response time under any operating conditions exceeds two minutes, probe service is indicated.

Summary of Operating Instructions

1. CALIBRATION

A. Switch instrument to OFF and adjust meter mechanical zero.
B. Switch to RED LINE and adjust.
C. Prepare probe for operation, plug into instrument, wait up to 15 minutes for probe to stabilize. Probe can be located in calibration chamber (see instruction manual) or ambient air.
D. Switch to ZERO and adjust.
E. Adjust SALINITY knob to FRESH.
F. Switch to TEMP and read.
G. Use probe temperature and true local atmospheric pressure (or feet above sea level) to determine correct calibration values from Table I and II.

EXAMPLE: Probe temperature = 21 C; Altitude = 1000 feet.

From Table I the calibration value for 21 C is 8.9 mg/L. From Table II the altitude factor for 1000 feet is approximately 0.96. The correct calibration value is:

8.9 mg/L X 0.96 factor = 8.54 mg/L

H Switch to desired dissolved oxygen range 0-5, 0-10, or 0-20 and with calibrate control adjust meter to correct calibration value determined in Step G.

Note: It is desirable to calibrate probe in a high humidity environment. See instruction manual for more detail on calibration and other instrument and probe characteristics.

2. MEASUREMENT

A. Adjust the SALINITY knob to the salinity of the sample.
B. Place the probe in the sample and provide stirring at a rate of about 1 foot per second.
C. When the temperature and DO reading have stabilized, switch to the appropriate range for better resolution, ensure stabilization, and read DO.
D. We recommend the instrument be left on between measurements to avoid necessity for repolarizing the probe and recalibrating the instrument.

3. GENERAL CARE

A. Replace the instrument batteries when unable to adjust to red line. Use (2) Eveready No. 935 "C" size or equivalent.
B. In the BATT CHECK position the voltage of the stirrer batteries is displayed on the red 0-10 scale. Do not discharge below 6.0 volts. Recharge for 14-16 hrs. with YSI No. 5728 charger.
C. Membrane will last indefinitely; depending on usage - average replacement is 2-4 weeks.
D. Properly store the probe: Short-term storage (less than 3 weeks) - the probe should be stored with electrolyte in humid environment to prevent drying out. Long-term storage the probe should be rinsed of electrolyte and stored dry with a membrane installed as a dust cover. Tag meter with "STORED DRY" date and initial.
E. Calibrate as needed, such as after instrument has been turned off or calibration checks so determine. Check calibration requently during use, especially after jarring movement and changes in altitude.

References

Instruction Manual - YSI Model 57 Dissolved Oxygen Meter

YSI 5700 Series Dissolved Oxygen Probes - Instructions

"Making Dissolved Oxygen Measurements" booklet by YSI

Conversation with YSI Technical Representative Linda Hart on 2/12/92 (1-800-765-4974 x235)

10. FREE & TOTAL CHLORINE PROTOCOL

Introduction

Chlorine and chlorine compounds are used in wastewater treatments as disinfectants. Disinfection refers to the selective destruction of disease-causing organisms.

Reactions in Water:

The most common chlorine compounds used in wastewater treatment plants are chlorine gas (Cl_2), sodium hypochlorite (NaOCl), chlorine dioxide (ClO_2), and calcium hypochlorite [$Ca(OCl)_2$].

When chlorine in the form of Cl_2 gas is added to water, two reactions take place: hydrolysis and ionization as

$$Cl_2 + H_2O <=======> HOCl \text{ (hypochlorous acid)} + H^+ + Cl^-$$
$$HOCl <=======> H^+ + OCl^- \text{ (hypochlorite ion)}$$

The quantity of HOCl and OCl^- that is present in water is called the *free (available) chlorine.* The relative distribution of these two species is very important because the killing efficiency of HOCl is about 40 to 80 times that of OCl^-. The percentage distributions of HOCl and OCl^- in water are very dependent on the pH and temperature (Metcalf and Eddy).

Reactions with Ammonia:

The effluent from most treatment plants contains significant amounts of nitrogen, usually in the form of ammonia and various combined organic forms. Because hypochlorous acid is very active oxidizing agent, it will react readily with ammonia to form three types of chloramines in the successive reactions:

$$NH_3 + HOCl \text{ ------> } NH_2Cl \text{ (monochloramine)} + H_2O$$
$$NH_2 + HOCl \text{ ------> } NHCl_2 \text{ (dichloramine)} + H_2O$$
$$NHCl_2 + HOCl \text{ ---> } NCl_3 \text{ (trichloramine or nitrogen trichloride)} + H_2O$$

These reactions are also very dependent on pH, temperature, contact time, and the ratio of chlorine to ammonia. These chloramines also serve as disinfectants, although they are extremely slow-reacting (Metcalf and Eddy). The chlorine in these compounds is called *combined (available) chlorine.* The *free chlorine* and *combined chlorine* compounds make *total chlorine.*

Sampling

Always hand grab samples are taken for immediate measurements. Priority pollutant sampling equipment cleaning is optional.

Measurements

Carry out all measurements as soon as grab samples are taken. Presently, there are two following methods used/available to determine free and total chlorine concentrations. Both methods are approved by the Environmental Protection Agency.

A: DPD* Colorimetric Method Using LaMotte Kits.
(* N,N-diethyl-p-phenylene-diamine, an indicator).

B: Hach DR100 Colorimeter.

METHOD A

Free Chlorine

1. Rinse a test tube with the water to be tested, refill the tube to the 10 mL line with the sample water.
2. Add one DPD #1 tablet, cap tube and shake to disintegrate tablet.
3. Immediately insert test tube into comparator and match color in tube against the color standards to obtain value.
4. This value represents the *free chlorine* content of the test sample in mg/L.

Note: Keep this sample if *total chlorine* is to be determined.

Total Chlorine

5. Add one DPD #3 tablet to the free chlorine test sample prepared above, cap tube and shake to disintegrate tablet.
6. Insert tube into comparator to obtain color match.
7. This resulting value represents the *total chlorine* in mg/L.

Note: Throughly clean and rinse test tube with distilled/deionized water after each test.

Advantage:(1) Quick;
Disadvantages:(1) Lower detection level/limit is limited to 0.1 mg/L, (2) Even moderate turbid sample can cause erroneous result.

METHOD B

TEST PROCEDURES

FREE CHLORINE, 0-2 mg/L

1. Open the light shield and turn the Right Set control fully clockwise.
2. Insert the 1-cm cell holder into the Left Set position of the sample well. Press down firmly to seat it in place. Close the light shield.
3. While holding the On button down, adjust the Left Set control to align the meter needle with the arrow at the far left of the scale arc.
4. Remove the cell holder and close the light shield.
5. Fill both 2.5-cm sample cells to the 10-mL mark with the water to be tested.
6. Open a DPD Free Chlorine Powder Pillow with the clippers. Add the contents to one of the 2.5-cm sample cells. Cap and shake for 20 seconds to mix. *See Note A.* If chlorine is present, a red color will develop. Do not allow more than one minute before completing Steps 7 through 10. *See Notes B and C.*
7. Cap the cell containing untreated water sample, open the light shield and place the cell into the sample well. Press down firmly to seat the sample cell. Close the light shield.
8. While holding the On button down, adjust the Right Set control for a reading of zero mg/L. Open the light shield and remove the sample cell.
9. Place the cell containing the prepared sample into the sample well. Press down firmly to seat the sample cell; then close the light shield.
10. While holding the On button down, allow the meter to stabilize. Read and record the mg/L free chlorine from the upper (2.5-cm) scale arc. *See Note D.*

FREE CHLORINE, 0-3.5 mg/L

1. Open the light shield and turn the Right Set control fully clockwise.
2. Insert the 1-cm cell holder in the Left Set position of the sample well. Press down firmly to seat it in place. Close the light shield.
3. While holding the On button down, adjust the Left Set control to align the meter needle with the arrow at the far left of the scale arc.
4. Rotate the cell holder to the Right Set position. Fill a clean 1-cm sample cell with the water to be tested. Cap the cell and place it into the holder. Close the light shield.
5. While holding the On button down, adjust the Right Set control for a reading of zero mg/L. Open the light shield and remove the cell.
6. Fill a clean 2.5-cm sample cell to the 10-mL mark with the water to be tested.
7. Open a DPD Free Chlorine Powder Pillow with the clippers and add the contents to the sample cell. Cap and shake for 20 seconds to mix. *See Note A.* If chlorine is present, a red color will develop. Do not allow more than one minute before completing Steps 8 and 9.
8. Fill a clean 1-cm sample cell with the solution prepared in Step 7.
9. Place the 1-cm sample cell containing treated sample into the colorimeter, close the light shield and press the On button until the meter stabilizes. Read and record the mg/L free chlorine from the lower (1-cm) scale arc. *See Note D.*

Notes, Free Chlorine

A. It is not necessary for all the particles to dissolve to obtain an accurate reading.

B. If the sample temporarily turns yellow when adding the DPD Free Chlorine Reagent or reads above the highest scale division, the free chlorine concentration is too high for the meter scale and a sample dilution is needed. A slight loss of chlorine may result from the dilution.

C. Samples should have a pH between 6 and 7. If necessary, an appropriate amount of acid or base that does not contain ammonium or chloride ions can be used (for example: 1.0N Sulfuric Acid Standard Solution, Hach Cat. No. 1270-37, or 1.0N Sodium Hydroxide, Cat. No. 1045-37). Test the sample immediately after adding the acid or base.

D. If the sample contains no free chlorine but some combined chlorine, the meter may drift to a continuously higher chlorine reading. If the meter comes to a stable reading within a few seconds, it may be assumed that only free chlorine is present.

TOTAL CHLORINE, 0-2 mg/L

1. Take a sample of the water to be tested by filling a clean 2.5-cm sample cell to the 10-mL mark.
2. Open a DPD Total Chlorine Powder Pillow with the clippers and add the contents to the sample cell. Cap the cell and shake for 20 seconds to mix. *See Notes A, B and C.* To allow time for proper color development, allow at least three minutes but not more than six minutes before completing Steps 3 through 8.
3. Open the light shield, turn the Right Set control fully clockwise and place the 1-cm cell holder in the Left Set position of the sample well. Press down firmly and close the light shield.
4. Hold the On button down while adjusting the Left Set control to align the meter needle with the arrow at the extreme left of the scale arc. Remove the cell holder.
5. Fill a clean 2.5-cm sample cell with the water to be tested. Cap the cell and place it into the sample well. Press down firmly to seat the sample cell. Close the light shield.
6. Hold the On button down while adjusting the Right Set control for a reading of zero mg/L. Open the light shield and remove the sample cell.
7. Place the cell containing the prepared sample into the sample well. Press down firmly to seat the sample cell; then close the light shield.
8. Hold the On button down until the meter stabilizes. Read and record the mg/L total chlorine from the upper (2.5-cm) scale arc.

TOTAL CHLORINE, 0-3.5 mg/L

1. Take a sample of the water to be tested by filling a clean 2.5-cm sample cell to the 10-mL mark.
2. Open a DPD Total Chlorine Powder Pillow with the clippers and add the contents to the sample cell. Cap the cell and shake for 20 seconds to mix. *See Notes A, B and C.* To allow time for proper color development, allow at least three minutes but not more than six minutes before completing Steps 3 through 8.

3. Open the light shield, turn the Right Set control fully clockwise and place the 1-cm cell holder in the Left Set position of the sample well. Press down firmly and close the light shield.
4. Hold the On button down while adjusting the Left Set control to align the meter needle with the arrow at the extreme left of the scale arc. Rotate the cell holder to the Right Set position.
5. Fill a clean 1-cm sample cell with the water to be tested. Cap the cell and place it into the cell holder.
6. Hold the On button down while adjusting the Right Set control for a reading of zero mg/L. Open the light shield and remove the sample well.
7. Fill a clean 1-cm sample cell with the solution from Step 2, cap the cell and place it into the cell holder.
8. Hold the On button down until the meter stabilizes. Read and record the mg/L total chlorine from the lower (1-cm) scale arc.

Notes, Total Chlorine

A. It is not necessary for all the reagent particles to dissolve to obtain an accurate reading.

B. If the sample temporarily turns yellow when adding the DPD Total Chlorine reagent or reads above the highest scale division, the chlorine concentration is too high for the meter scale and the sample must be diluted with deionized water. A slight loss of chlorine may result from the dilution.

C. Samples should have a pH between 6 and 7. If necessary, an appropriate amount of an acid or base that does not contain ammonium or chloride ions can be used (for example: 1.0N Sulfuric Acid Standard Solution, Hach Cat. No. 1270-37, or 1.0N Sodium Hydroxide, Cat. No. 1045-37). Test the sample immediately after adding the acid or base.

Advantages: (1) accuracy, (2) wider range;
Disadvantages: More time consuming than method A

References

Lamotte Kit.

Hach Company DR100 Colorimetric Manual.

Metcalf & Eddy. Wastewater Enginering, 3rd ed., New York 1991, pp 332-340

11. OIL & GREASE PROTOCOL

Introduction

Unlike some constituents that represent distinct chemical elements, ions, or compounds, oils and greases are defined by the method used for their determination. Oil & grease tests measure all material recovered as a substance soluble in a nonpolar solvent under acidic conditions. It is important to understand that an absolute quantity of a specific substance is not measured. No known solvent will dissolve selectively only oil & grease. Trichlorotrifluoroethane is the solvent of choice; the test is referred to as Freon-extractable.

Oil & grease includes such compounds as hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related industrial compounds not volatilized at temperatures below 70 degrees C. This may include sulfur compounds, certain organic dyes, and chlorophyll. The method is not applicable to the measurement of light hydrocarbons (e.g., petroleum fuels from gasoline through #2 fuel oils are partially lost and not accurately analyzed).

Equipment

Pre-cleaned 1-liter, wide-mouth glass jars; those provided by our lab.

Sampling Procedure

The most important consideration to keep in mind is that oil and grease adhere to sampling equipment, so <u>do not</u>:

- rinse the jar with sample before filling;
- fill the jar from a composited sample container;
- use our "bucket on a telescopic pole" equipment to obtain a hard-to-get sample, which is then poured into the jar; or
- pour out some of the sample if the jar was overfilled.

Fill the 1-liter jar only 3/4 full. This instruction will be printed with orange crayon on the lid of the jar.

Sampling of any wastestream with immiscible fluids requires special attention. It is simple to find a place in the wastestream where oil and grease are floating and to obtain a sample. Special attention is needed to ensure that the sample is representative, such that an accurate determination will be made of the quantity of oil and grease flowing per day.

Neither skimming from the surface nor dipping deep into the wastestream with the jar will produce a representative sample, in most cases. Find a place in the wastestream where mild turbulence is present which can provide some vertical mixing. At a wastewater treatment plant this may be a wier or flume.

Another approach may be used when estimating larger volumes. Divert a measurable quantity of the wastestream into a container. After allowing the two fluids to separate, it will be possible to measure the thickness of the oil layer and determine the volume of oil present.

References

APHA, et al., Standard Methods, 17th Edition.

Puget Sound Protocols, 1989.

12. METHODS FOR ESTIMATING STREAMFLOW

Estimating Discharge In Streams and Channels

The importance of obtaining good hydrological information can not be overem-phasized. Accurate discharge measurements link precipitation to runoff and allow calculation of pollutant loadings. The hydrologic character of a stream and its change through time can be important indicators of the effects of development or stormwater controls.

A. Development of a Gaging Station

A staff gaging station should be set up at the mouth of the watershed. The purpose of the gaging station is to develop a relationship between stream height (stage) and flow. Once this relationship is established, it will no longer be necessary to measure flow with a rod and current meter each sampling trip. Further, the information (used in conjunction with precipitation data) can be used to estimate changes in stream flows as watersheds develop. (Note: It is possible a gaging station already exists on a watershed. The USGS has established a network of gaging stations throughout the country. Contact the USGS Water Resources Division in Tacoma [telephone (206) 593-6510] for information on gaging station locations.)

1. Site Selection Criteria

It is important to select a proper location to establish a staff gage station or a flow monitoring site. Proper site selection will improve the accuracy of flow measurements at all stream discharge levels. The following criteria should be considered when establishing a discharge measurement station; however, it is rarely possible to meet all the criteria recommended here. Be aware of the limitations of the site selected and possible effects on measurements.

a. Stream Reach Criteria

(1) The stream should be straight for 300 feet upstream and downstream of the discharge site.

(2) Flow is confined to one channel at all stages of discharge (i.e., there are no surface or subsurface bypasses, up to bankfull flow).

(3) Stream bed is subject to minimal scour and relatively free of plant growth.

(4) Stream banks are stable, high enough to contain maximum flows, and free of brush.

(5) Gaging stations should be located a sufficient distance upstream of tributaries and tidal action to prevent these from affecting stage/discharge measurements.

(6) All discharge stages should be measurable somewhere within the reach (it is not necessary to measure low and high flows at the exact same cross-section).

(7) The site should be readily and safely accessible.

b. Cross-section Criteria

In selecting a cross-section within a stream reach, consider the following:

(1) Stream banks should be relatively high and stable.

(2) A straight section of the stream should be chosen, where stream banks are parallel to each other.

(3) Depth and velocity must meet minimum requirements of the method and instrument being used.

(4) The stream bed should be relatively uniform with few boulders or heavy aquatic plant growth.

(5) Flow should be uniform and free of eddies, slack water, and excessive turbulence.

(6) Sites downstream of rapid changes in stage and velocity should be avoided.

2. Setting Up a Staff Gage

a. Attach staff gage vertically on a permanent structure (concrete piling, revetment, etc.).

b. Set the zero point of the staff gage below the lowest level of stream flow to prevent negative values of gage height.

c. Establish a datum point on the gage, and make two or three reference marks at the same level on nearby permanent features. (Use a point on the gage that is above the highest expected gage height to prevent flow-related erosion of the marks.) The datum may also be referenced to an official surveyors benchmark. By establishing reference elevations, the datum can be recovered if the staff gage is destroyed.

d. Set the gage datum to an accuracy criterion of 0.01 feet and recheck it at least every two to three years.

e. Establish a stage/discharge rating curve (see next section)-

3. Establishing a Rating Curve

a. Take stream flow measurements over a wide range of gage heights. It will be easy to establish data points for average stream flows, but the relationship will not hold for high and low flows. Consequently, it is very important to get measurements during high and low stream flows so that a wide range of conditions is represented on the rating curve. Ideally, measurenents for low, average and high flows should be separated by an order of magnitude.

b. Note the gage height both before and after measuring flow. (If wave action occurs, read height as the average of the elevations of peaks and troughs.)

c. Plot calculated stream flow (x-axis) versus gage height (y-axis). Provide a sufficient number of points to allow a smooth curve to be drawn through the points. As noted above, be sure the high and low ends of the curve are represented in the relationship.

d. Make periodic checks of the discharge curve, especially after high waters or floods. Recalibrate the curve if checks indicate the stream flow/gage height relationship has changed, usually due to significant sediment deposition or erosion of the stream bed.

NOTE: Stream height can also be measured as the distance from the surface of the water to a permanent point above the stream. A bridge provides a convenient place for these measurements. Make a permanent mark on the bridge so stream height is always measured from the same location. Lower a marked, weighted tape until the weight just touches the water surface. Record the distance. Use this

measurement as the gage height in establishing the rating curve. As with an instream gage, this method assumes there is no change in the bottom profile of the cross-section. Check the profile periodically-

B. Stream Flow Measurement Techniques

Current Meters:

There are two different types of current meters available in the strorage area: a Marsh-McBirney, Inc. model 201 portable water current meter, and a Swoffer Instruments, Inc. model 2100 instrument. The instruction manuals for these instruments are available in the equipment room. The following is a short summary of the operation and maintaince for these instruments

Swoffer Model 2100:

The Swoffer is composed of a rotor assembly, sensor body, and cable which are attached to a wading rod (assembly is called the Sensor Wand), an indicator panal then attaches to the Sensor Wand to form the whole unit.

1. Remove the sensor protection cap and install the propeller rotor using the Rotor Installation Wrench provided (these should be located in the back of Indicator box).

2. Connect the Sensor Wand to the Model 2100 Indicator by using the twist lock connector.

3. Rotate the Indicator master switch to the Calibrate position. It should read about 186 fps or 610 m/sec. Change to whichever unit of measure is wanted by use of the **feet/meters** switch located inside the battery compartment.

4. Rotate the selector switch to the minimum update time.

5. Place the propeller in the stream with the propeller facing into the stream flow.

6. The wading rod should be set to the appropriate depth (see MEASURING STREAM VELOCITY).

7. Press and release the **reset** button to zero the display.

8. The next figure which appears on the display will be the stream velocity.

Marsh-McBirney Model 201:

The Marsh-McBirney consists of a transducer probe with cable, and a signal processor. The Marsh-McBirney wading rod has an adapter capable of holding the transducer probe.

1. Attach transducer probe to wading rod.

2. Set selector switch to **Cal** and the time constant switch to 2. After approximately 10 sec., the readout should be on or between 9.8 and 10.2. If not, change the bateries and recheck.

3. Set selector to desired measuring unit (e.g., FT/SEC).

4. Set time constant switch.

   The purpose of the time constant is to help stabilize flow readings. This produces a delay between the time the unit is first turned on and the time the first full scale reading is reached. This delay can be calculated as seconds by multipling the switch setting by five. Start with the smallest time constant **2** (10 second delay). If after the calculated time delay the output has not stabilized, move to the next highest number.

5. Place the probe in the stream with the round end of the sensor facing into the stream.

6. The wading rod should be set to the appropriate depth (see MEASURING STREAM VELOCITY).

7. Wait for the appropriate time delay then record stream velocity.

****

1. Current meter measurements

   a. Select an appropriate cross-section.

   b. String measuring tape at right angles to the direction of flow and measure the width of the cross-section. (Leave the tape strung across the stream.)

c. Divide the width into approximately 20 points of measurement. (If previous flow measurements have shown uniform depth and velocity, fewer points may be used. Smaller streams may also require fewer points.) Measuring points should be closer where depths or velocities are more variable. Cross-sections with uniform depth and velocity can have equal spacing.

d. At each of the measuring points:

(1) Record the distance from the initial starting bank

(2) Record the depth

(3) Record the velocity using a current meter. (See Following Notes)

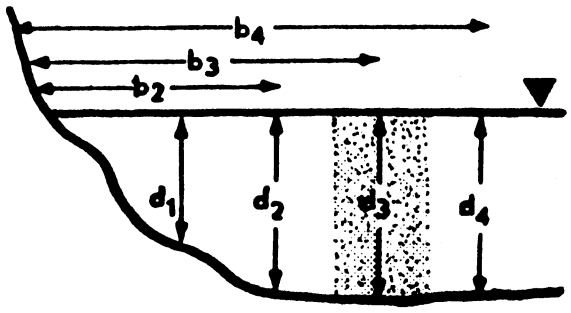
MEASURING STREAM VELOCITY: Stream velocity varies horizontally (from left bank to right bank) and vertically (top to bottom). Horizontal differences are accounted for by measuring velocity along a cross section of the stream, as described above. To correct for vertical differences, hydrologists have developed a standard technique to ensure consistency in determining average velocity. This technique assumes that the "average" vertical stream velocity occurs at some percentage of the stream depth. This percentage changes with stream depth. In streams where the maximum depth is 2.0 feet or less, the average stream velocity is assumed to occur at six-tenths of total depth (as measured from the surface). In streams deeper than 2.0 feet, the velocity is measured at two-tenths and eight-tenths of the total depth. Velocity is calculated as the average of these two measurements.

(4) Calculate discharge as a summation of discharge in partial areas. Compute discharge in a partial area using the equation:

$$q_3 = v_3 d_3 (b_4 - b_2)/2$$

where:
b_2 = distance from initial point to the preceding point (feet)
b_4 = distance from initial point to the following point (feet)
d_3 = mean depth of partial area 3 (feet)
v_3 = average velocity in partial area 3 (feet)
q_3 = discharge in partial area 3 (cfs)

Variables are illustrated below:



generalized equation:

$$q_x = v_x d_x (b_{x+1} - b_{x-1})/2$$

2. Float Method

When usual flow measurement methods cannot be used (e.g., during extremely high flows, or when equipment is not available), a floating object can be used to estimate velocity. The object can be an orange, a plastic sample bottle partially filled with water, or other semi-buoyant object.

a. Locate a straight stretch of stream.

b. Select two cross-sections within the stretch, measure (or estimate) their cross-sectional area and distance between them. (Sites should be far enough apart that float movement between sites exceeds 20 seconds.)

c. Release the float at the upstream site and record the time it takes to reach the downstream site. Repeat twice and average the three measurements. To increase accuracy, release the float at different places across the width of the stream.

d. Calculate the velocity as distance travelled divided by average travel time.

e. Calculate the adjusted (true mid-depth) mean velocity of the water by multiplying the surface velocity by 0.85.

f. Calculate discharge by multiplying velocity by the average cross-sectional area.

Measuring Flow From Pipes

The flow measurement techniques described above also work for pipe discharges under certain conditions; e.g., if there is upstream access to release the float or tracer. However, often it is not possible to use these techniques with a pipe. The following methods can be used to estimate pipe discharge.

A. Volumetric Measurement

In this method discharge is calculated by observing the time required to fill a container of known volume. A limiting factor of this technique is that it can only be used with small discharges (i.e., where all of the flow can be caught in one container). This technique can also be used to estimate discharge over a weir or at any place where flow is concentrated into a narrow stream.

1. Place bucket or other container below the discharge.

2. Time how long it takes to fill the container. Repeat three times (or more if there is a large difference between results). Whenever possible, the time interval should exceed 20 seconds.

3. Calculate discharge as the volume of the container divided by the average time to fill it.

B. Discharge of a Jet of Water

This technique can be used on any discharge regardless of size. The limitations are that the pipe must be horizontal and the fluid must be confined on all sides (e.g., a pipe, the pipe must be running full, and the fluid must be in free fall). See illustration next page:

1. Measure or estimate the diameter of the pipe.

2. Measure the distance from the end of the pipe to the spot where the stream of water hits ground ("x").

3. Measure the vertical distance from "x" to the midpoint of the pipe orifice ("y").

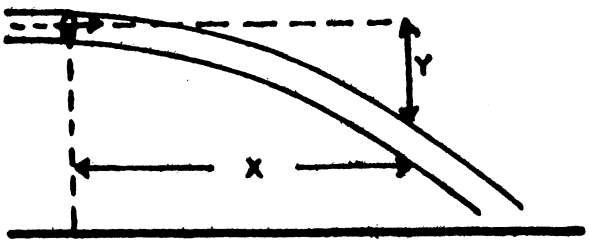
4. Calculate the velocity ("v") as:

$$V = 4.01(x)/\sqrt{y}$$

5. Calculate the area ("A") of the pipe as:

$$A = \pi r^2$$

6. Calculate the discharge volume by multiplying area by velocity. Units of measurement must be the same.



C. Dilution Method

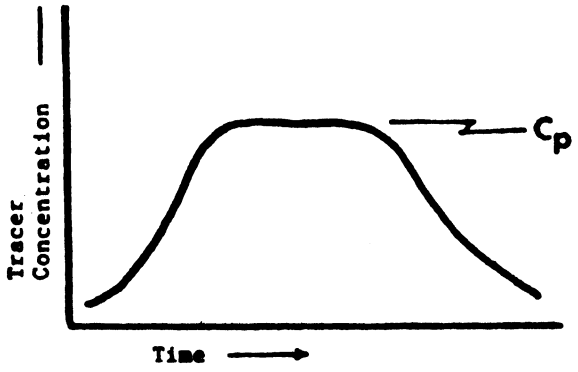
Use common salt, fluorescein or rhodamine dye, or any easily measurable material not present in the stream and not likely to be lost by chemical or biological reactions. (Do not use any material that may damage the stream environment. The USGS recommends use of rhodamine wt dye because it is relatively unaffected by photosynthesis and adsorption and is minimally toxic compared to other common dyes.) Two methods are presented here. The first requires a constant-rate injection of the solution, the second allows for the solution to be "dumped" at one time. For both methods, it may be necessary to estimate the amount or concentration of tracer material needed, to minimize cost and possible environmental effects. The necessary computations are described in "Measurement of Discharge by Dye-dilution Methods" (USGS, 1965).

1. Constant-rate injection

   a. A known concentration of tracer material is injected into the stream at a constant rate (q) for a given period of time.

   b. Samples are collected at a site far enough downstream to ensure complete mixing of the tracer with receiving water. Sufficient samples must be collected to form a concentration-time curve as shown below.

   c. The peak concentration (C_p) is estimated from the concentration-time curve.



   d. Stream discharge (Q) is calculated as:

$$Q = q[C_s-C_p)/(C_p-C_b)]$$

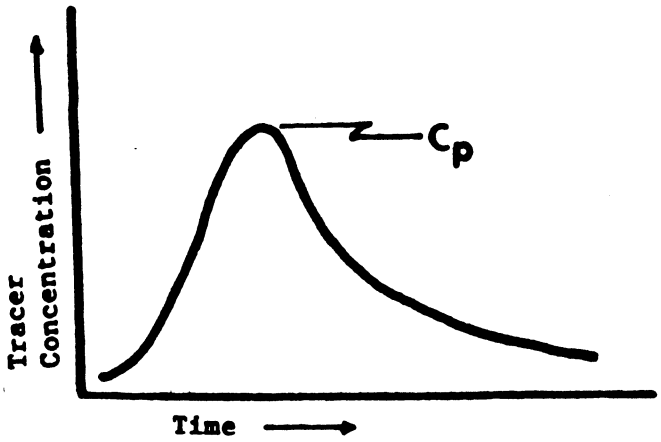
Where: Q, q, and C_p are defined above

C_s = Initial concentration of tracer
C_b = Background (stream concentration of tracer

2. Sudden-dump Method

   a. A known concentration of a tracer solution is dumped into the stream.

   b. Samples are collected far enough downstream to ensure complete mixing of tracer in the stream. Collect enough samples at an appropriate frequency to develop a concentration-time curve as shown below:



c. The stream discharge (Q) is calculated as:

$$Q = (V_s * C_s)/[\int_0^\infty (C-C_b)dt]$$

Where: Q, C_s, and Cb are defined above iu#1

V_s = Volume of tracer solution introduced
C = Tracer solution concentration at a given time

The term $(C - C_b)dt$ can be approximated by the term:

$$\sum_{i=1}^{N} (C_i-C_b)\ (T_{i+1}-T_{i-1})/2$$

Where: C and C_b are defined above

i = sequence number of the sample
N = the total number of samples
T_i = time when sample C_i was taken
T_{i+1} = time when sample following sample C_i was taken (C_{i+1})
T_{i-1} = time when sample preceding sample C_i was taken (C_{i-1})

The final concentration of the tracer in the stream needs to be accurately measured in either of these methods.

13. CALIBRATION AND DEPLOYMENT OF HYDROLAB® MULTIPARAMETER METERS: SURVEYOR 2 AND DATASONDE 3

Introduction

The Surveyor® 2 (S2) and the Datasonde® 3 (DS3) are multiparameter water quality monitoring instruments produced by the Hydrolab Corporation. Detailed information on these units are available in the appropriate Operating Manual (OM). Hydrolab also provides excellent support; a technician can be contacted at 1-800-949-3766. These protocols summarize calibration and deployment methods commonly used by WAS. Procedures are categorized as either common to all units, or specific to the S2 or DS3. Not all potential applications of these units are described here.

The S2 is deployed by cable and can measure temperature, pH, dissolved oxygen, conductivity, redox potential, salinity, and depth. Readings are transmitted to a remote display unit, from which the sampler may transcribe results to a fieldbook. This unit is best for multiparameter vertical or horizontal profiles and spot measurements by boat, wading, or from bridges.

The DS3 measures the same parameters as the S2 (except for redox), and also can calculate several other secondary parameters, such as percent oxygen saturation and total dissolved solids. The DS3 is equipped with an internal computer and battery pack for remote deployment, monitoring, and datalogging. This unit is somewhat heavier than the S2, and is used for collecting a time series of data at a single location. A Surveyor 3 Display/Logger unit is available that allows cable deployment and direct readings from a DS3 in a fashion similar to the S2, except that the S3 unit has internal logging capabilities.

Calibration of the Units

All: Calibration and Maintenance Logs are maintained for both the S2s and the DS3s. Record all calibration and postcalibration information in these logs. Also note any maintenance activities in the logs. This assists both in providing information on the history of use and in identifying any patterns of poor performance.

Calibration takes about 45 minutes per meter (if you know what you're doing and no unexpected problems arise). Post-calibration is a little faster, not counting the analysis of any Winklers collected for field verification.

Calibration of pH, conductivity, dissolved oxygen, and depth are addressed here. Temperature is factory calibrated, but can be checked against a standard, if desired. It is best to calibrate the

meter at the same altitude as the survey site. For sites well above sea level, this may mean taking a field DO kit and pH buffers with you in the field. Remember to standardize the thiosulfate before you depart, and check it again when you return.

Begin by assembling the units. Take off storage cup and examine the probes. Check the DO membrane for damage, the conductivity probes for corrosion, and the pH probes for fouling. (Routine cleaning and maintenance is suggested unless the unit has been recently maintained or in use with satisfactory results. Consult OM for maintenance procedures. If DO membrane is changed, leave probe to soak for at least 24 hours before calibrating.) Screw on the stirrer.

S2: Attach the two underwater cable connectors to the stirrer and transmitter (upper part of meter). Attach cable to display unit. Attach a charged gel-cell battery to the display unit. Turn unit on and switch to temperature setting. Let temperature reading stabilize.

DS3: Boot up the laptop computer. Using the computer patch cable, plug one end in the serial port of the computer, and connect the other ends to a battery and to the landward end of the cable. Connect the underwater ends of the cable to the stirrer and transmitter of one of the units. The unit should begin to "tweet". (The "buzzer" that tweets can be toggled off, but the tweeting is useful to confirm operation of the unit.) One unit at a time is connected to the computer, and each unit is connected in turn for the procedures described here.

Insert disk with the modem program, and change the computer directory to A:\. Type "XTALK" to start the modem program. (Crosstalk commands will be discussed here, but other modem programs such as PROCOMM could be used. Commands are shown in caps, but lower case is acceptable.) Request "STD" command file. Press "escape" to get command prompt and type "GO LO". The DS3 should now be displaying lines of data on the computer screen. This is called "Standard Operating Mode" or SOM. Let temperature stabilize.

The parameters displayed in SOM will be the parameters that will be recorded during logging. Parameters may be added or removed, or the units employed may be changed. Consult the OM for details.

All: Check that the stirrer is turning quickly and quietly. Proper operation of the stirrer is necessary for maximum accuracy, and poor stirring may result in strange (typically unusually high) readings of DO. Pull off the magnetic stirrer and check for fouling. Relubricate with silicone lubricant if desired, and especially if the stirrer makes a grinding noise or spins slowly. A very light coating seems to do best to achieve maximum speed and minimum chatter.

Put the units in the aerated water bath.

Dissolved Oxygen

All: The preferred method by EILS for dissolved oxygen (DO) calibration is by comparing readings in a saturated water bath to the oxygen measured by Winkler titrations. Two other methods in the manuals recommend calibrating to theoretical values of air saturated water and water saturated air. Calibrating to saturation values is acceptable in situations where use of the Winkler is too slow or not possible. However, the Winkler titration method is recommended and discussed below, because it is routinely used at EILS and offers actual (as opposed to theoretical) values. Consult the OM for the saturation methods.

S2: Ensure that temperature and DO readings are stable. Take a pair of water samples from the water bath and determine the oxygen concentration by Winkler titration (see the Chapter 8 - "Dissolved Oxygen - Winkler Titration"). Using the "slope" toggle, change the DO reading to the mean value of the two titrated samples. To save the calibration, turn switch to "battery" and pull both calibration toggles down until display reads "save". YOU MUST SAVE THE CALIBRATION TO KEEP THE NEW CALIBRATION IN EFFECT AFTER THE UNIT IS TURNED OFF. (Saving the calibration after each parameter is completed will reduce your agony in the event that you accidently turning off the machine before all parameters have been calibrated.)

DS3: Measure water bath oxygen by Winkler method. Move cable to a different unit and let meter operate for two minutes. Calibrating at two minutes is recommended, because the meter will warm up for two minutes when recording in the field. Providing a longer warm-up time during calibration may not realistically represent values measured in the field. After calibrating the meter, move cables to the next meter and repeat.

Calibrate meter by pushing "space" to call up menu, and follow menu instruction for calibrating DO. The atmospheric pressure requested will calculate the percent saturation for measured conditions. You can call the local National Weather Service station if you like, or just input a typical value - 760 for near sea level or an adjusted value for higher elevations. Enter measured DO, and you're done - the calibration is automatically saved.

Saturation and Air Calibration: Calibrate using "%" menu item in "Calibrate", and enter "100%". This is a very quick way to calibrate the DS3, but use of the Winkler is recommended because the method is probably more accurate and similar to field conditions.

Conductivity and pH

All: These methods are discussed together, since the procedures are very similar. A conductivity standard should be used that is close to the conditions expected in the field. KCl standards of 100 and 1000 umho/cm are available through a vendor such as VWR. These standards should be fresh, i.e. unopened or only recently opened, since the conductivity of the standard changes when exposed to air, and has a poor shelf life in general. Refrigeration of the conductivity standard improves its shelf life. Two standards for pH are needed, pH 7 and either 4 or 10, depending on the field conditions expected. Use of low-ionic strength standards for freshwater deployment is recommended.

For fresh water (less than 1500 umho/cm), use of the "D5" conductivity cell block is recommended. This cell block has large holes in the front; the standard block used for higher conductivity is solid with small holes at the top.

Remove the unit from the water bath. Unscrew the stirrer and set aside. Screw in the calibration cup. Fill the cup half full of DI water, put on cap, swish, and dump. Repeat. Fill the cup with a centimeter or so of standard, swish and dump. Repeat. Put the clamp stand in the sink and attach the meter probes upward. Fill the cup with standard, and observe readings. Calibrate pH first with 7, and then with the 4 or 10. All units provide internal temperature compensation for both pH and conductivity, so calibrate to the 25° standard value.

Since the standards are quite expensive, if you anticipate using large quantities you should save and reuse the standard after the final soak. Use the old standard for the rinses, discarding after each rinse. Then fill the cup with the rest of the old standard, topping off with fresh standard, and save that standard for the next time.

S2: Check temperature for stable readings. Then observe pH and wait for a stable reading. The first pH readings are often slow to stabilize. One possible method is to wait for a reading to remain constant for 30 seconds. Adjust the meter to the 25° standard value, using first the "zero" toggle for the neutral standard, and then the "slope" toggle for the acid or base standard. For a more precise calibration, check back to pH 7 to make sure it still reads right after the slope adjustment. If it doesn't agree, repeat the calibration procedure. When the calibration is satisfactory, SAVE THE CALIBRATION!

For conductivity, adjust the reading with the "slope" toggle, and the SAVE. Note that when using the D5 cell block, the readings displayed are five times the true value.

DS3: Remove the black cap on the pH reference electrode. Follow the procedures for rinsing and filling with standard. Let the standard set in the cup for two minutes and then calibrate using the computer menu. Begin with the neutral standard, and then the acid or base standard.

For conductivity, make sure the meter is programmed for the correct conductivity cell block (under "variables/conductance/fresh" or "/salt"). The computer internally calculates the correct reading.

Depth

All: Calibrate depth either by holding meter at surface and calibrating to zero, or by using a marked cable and calibrating to a known depth.

S2: Change displayed depth to correct value with "zero" toggle. DO NOT SAVE. Depth is calibrated in the field, and must be recalibrated every time the meter is turned off.

DS3: Depth is calibrated in the lab using the menu.

Deployment of Meters

All: Probes should always be stored in tap water so that they do not dry out when not in use. A storage cup filled with water may be used, but usually the stirrer is reattached and the meter is set in a tube filled with water set in a carrying crate.

Beware of deploying the meters in waters with filamentous algae or plant growth, as this may foul the stirrer. Extremely turbid or slimy waters may foul the DO membrane, so inspect frequently in those conditions. Avoid using the Hydrolab in turbid water, or letting the probes enter sediment deposits. This will extend the life of the unit.

Anoxic waters have the potential to "poison" the DO probe by plating the platinum probe with sulfur compounds. The Hydrolab instruments have proven to be resilient to this problem, but keep the probes in anoxic water for the absolute minimum amount of time necessary.

Use a great deal of care with the cables. The power cables are notoriously weak, and should be handled gently. The sonde cables and deployment cable must not be crushed or bent sharply. Do not ever hang weights on a Hydrolab. If a unit gets caught on an underwater snag, use great care and finesse to ease it loose. Better yet, try to avoid areas suspected of containing a lot of underwater debris.

Field verification of readings with other methods is usually desirable, especially for oxygen. Take verification samples for analysis of DO by the Winkler method. If desired, pH and conductivity can be verified either with a different meter (YSI, Beckman, Orion, etc.) or by laboratory analysis. An occasional duplicate profile may be desirable, too.

A reasonable frequency of DO field verification is to take a Winkler at the beginning, middle,

and end of the day or logging run. Take samples from several depths, if possible. Take a set of duplicates at one station.

S2: Meter may be turned off. Turning the meter on ten minutes or more before field use is recommended, since this may shorten equilibration time. Also, once in the field, fill the carrying tube with water from the study waters, if it is fresh and fairly clear. Transport in salt water is not recommended since it is so corrosive. Protect the battery and display unit from excessive moisture, such as rain or spray.

To take reading, place in water. Calibrate depth, if desired. Swish meter, or in swift streams turn slowly, to remove air bubbles that may disturb conductivity readings. Check temperature first for stable readings, and then pH. As with all environmental measurements, choosing the "true" value from unstable measurements is often a challenge and an art. Of course, you should also check that your anchor is holding or that you are not in an area of active mixing from some input.

A fully charged battery should be adequate for a full days' operation. A flashing display or error message may indicate a low battery or other more serious problems. The "IorE" message indicates a loose wire, which may be corrected by wiggling or tightening, or may mean factory repair is necessary. Partial numbers or gibberish may indicate water in the sonde, which is an extremely serious situation. Note the message that was displayed, and cease using the meter until the problem is resolved. Continued use of a meter with electrical problems or with a leak may cause damage that is very expensive to correct.

DS3: To program a logging run, go into "logging setup" from the menu. Only four runs may be stored at a time, so you may have to erase an old file with "logging erase". Needless to say, make sure the logging results are stored somewhere else before erasing a file. Setting up a run to start a little before you intend to deploy the meter allows you to hear the beeps of the first power-up to confirm operation. Set the run to continue as late as you possibly will retrieve the meter. This allows some padding to account for delays in deploying the meter at the time you intended.

Disconnect the battery from the computer and enter "logging status". This will give you an estimate of internal battery life. As a rough rule of thumb, three readings of the DO probe with stirrer uses about 1% of the battery life. If the status check indicates less than 30% of battery life left at the end of the logging runs, you may want to put in fresh batteries as a precaution.

To replace batteries, carefully unscrew the Allen bolts on the top of the transmitter. The battery pack is waterproof and spring-loaded. Replace the 10 AA Cells. Clean and relubricate the O-rings with silicone lubricant before refastening the battery pack.

Before putting the meter in the transport tube, don't forget to put that black cap back on the pH reference electrode! Pack up the computer and cables, and attach the stirrer to the transmitter with the short remote deployment cable. Bring the dedicated Hydrolab tool box, which should have pliers and Allen wrenches, extra parts, and the shackles for the buoys. The buoy cable should be in assorted lengths in the transport crate, along with a pair of leather work gloves. Pier blocks are used for anchors, and they are quite heavy to discourage tampering. The white foam buoys have a short length of cable with a loop attached.

You may wish to check the meters in the field before deployment. The portable computer should have a dashboard (cigarette lighter) adapter plug and a patch cord for communication between the computer and the meter. Bring an extra gel-cell to save the internal batteries. Check under "logging/review" to see readings already stored in the logging run files.

Pick a deployment site that is relatively isolated, if possible. Best sites are probably distant from boat launches, bridges, navigation channels, fishing spots, swimming holes, roads, waterfront homes, docks, or other signs of access. Check the depth with an S2, Secchi disk, calibrated anchor rope or whatever. Cables are marked at the loops with the length. It never hurts to have extra - slack is desirable for tidal changes or unexpected rises in the river, and excessive slack can be looped and held with a clamp. Also take into consideration how far the meter will drift at low tide and if currents or wind push the meter in any direction.

Using the shackles with the Allen wrench bolts, attach the cable and meter to the short loop on the buoy, and the anchor to the other end of the cable. Take off that stupid black cap from the pH electrode! Put the meter in the water, swish away bubbles, let it hang from the buoy, and move it to the side. Carefully and slowly lower in the anchor. Don't get your fingers caught or lose your balance, if possible. Use the roller attached to the jet sled or the deployment boom on the whaler to make this job easier and safer. If the boat has drifted and the anchor hasn't hit bottom, you may want to hold the anchor off the bottom and swing the boat closer to the shore. Having a beefy young intern is very useful for deployment and retrieval, but not always available, so enjoy the exercise. Throwing the anchor in, only to see the meter and buoy plunge out of sight, must be an unsettling experience.

For marine deployments, a different rig can be used, where the meter is held a constant distance off the bottom by a submerged buoy and a retrieval line and buoy floats on the surface. Again, avoid high traffic areas where dragging anchors or fishing lines are possible.

Take a Winkler field verification sample after you have deployed the meter, and again when it is retrieved. Timing the sampling to coincide exactly with the logging time is best, but sometimes tricky. An alternative is to deploy the meter, continue with other work, and then return to collect verification samples between two meter readings. Similarly when retrieving, take the verification samples, do something else until the meter takes another reading, and then

retrieve the meter. Verification samples taken as deep as you can reach may be acceptable, but in some situations (e.g. rapidly changing parameter gradients with depth) use of a Van Dorn at the depth of the probes may be more representative.

When you retrieve the meter, put the doggone black cap back on, filled with electrolyte!

Postcalibration

All: Post-calibration is accomplished in the same manner as calibration, with differences noted below. Postcalibration of DO is a little easier than calibration, since Winkler samples from the bath can be fixed, the meter reading immediately recorded, and the Winklers titrated and the results recorded at your leisure.

S2: Note readings of all parameters in the Log.

DS3: Take the black cap off. Note the reading that appears in the SOM after two minutes of operation. Rotate the meters being monitored to approximate the two-minute warm-up of field conditions.

Download files by using "logging/dump" from the menu. "Spreadsheet importable" will give you a file easily imported to Lotus 123. Use "Follow calibration" if you calibrated after programming the logging runs, but use "Setup calibration" if you recalibrated during postcalibration. When the computer indicates "Beginning XModem Transfer", time is of the essence. Press "escape" to get the command prompt, and type "rx 'filename'". Use a ".PRN" extension for easy 123 import. The file will be sent to the disk in A: drive. If you take too long, time will expire, so just try again!

All: If DO post-calibration has drifted significantly (>0.2 mg/L): the membrane may need to be replaced; the pre-calibration was poor or was not saved; or postcalibration occurred long enough after calibration and deployment to allow some drift. If pH post-calibration has drifted significantly (>0.1): replace reference electrode solution; use fresh standard buffer; clean all probes. If conductivity has drifted significantly: polish and clean the electrodes.

Before storage, put the black cap filled with electrolyte on the DS3. To store, put tap water in the storage cup and attach over the probes. Wash and wipe the meter and stirrer off. Put the dummy covers on the cable plugs. Return to a dry transport tube. Put gel-cells on the charger. Thank the meters and pat them for a job well done.